Carbohydrate *C*-Sulfonyl Chlorides for the Simple, Convenient Access to Glycoconjugates

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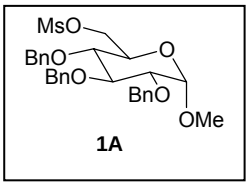
Supporting Information

Organic synthesis.

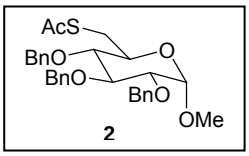
General. Reactions in anhydrous solvents were all performed using oven dried glassware under an atmosphere of argon. Reagent grade solvents were all purchased from chemical companies and used without prior purification. Anhydrous THF, ether, toluene, CH_3CN and CH_2Cl_2 were dried and purified through activated alumina columns as described.[1] D*iiso*propylamine, triethylamine and pyridine were distilled from KOH. For chromatographic purification, technical grade solvents were distillated prior to use. TLC was performed using Machery-Nagel Alugram Sil G/UV_{254} TLC plates and visualized with ultraviolet light at 254 nm followed by ceric ammonium molybdate, phosphomolybdic acid or H_2SO_4/MeOH stains. Chromatographic purification of products was accomplished by dry column vacuum chromatography[2] on either Merck Silica Gel 60 (15 - 40 µm) or Brunschwig silica 18-32, 60Å (18-32 µM). Concentration under reduced pressure was performed by rotary evaporation at 40°C and the purified compounds were subsequently dried under high vacuum (<0.5 Torr). NMR spectra were recorded on a Varian Mercury 300MHz apparatus operating at 300 MHz, 75 MHz and 282 MHz for ^1H, ^{13}C/DEPT and ^{19}F, respectively, and chemical shifts (δ) were referenced to the internal solvent signals for ^1H and ^{13}C. Multiplicities are reported as follows: ^1H: s = singlet, d = dublet, t = triplet, q = quartet, m = multiplet; ^{13}C: C, CH, CH_2, CH_3 (determined by DEPT); coupling constants are reported in Hz. IR-Spectra were recorded in $CHCl_3$ on a Perkin Elmer Spectrum RX I FT-IR apparatus (thin films on NaCl plates) and are reported as absorption maxima in cm^{-1}. Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium at the ETH, Zürich. High resolution matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) and electrospray ionization (ESI-MS) were performed by the mass spectrometry service of the LOC at the ETH, Zürich.



1A

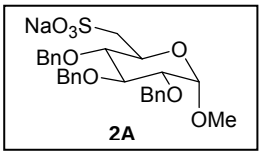
Mesylate 1A. Alcohol **1**[3] (1.181 g, 2.54 mmol) was dissolved in anhydrous CH_2Cl_2 (25 mL) at 0°C, anhydrous pyridine (3.0 mL) followed by MsCl (0.50 mL, 6.4 mmol) were added and the solution was stirred at 0°C for 1 h and at room temperature for 7 h followed by addition of sat. aq. $NaHCO_3$ (50 mL). The layers were separated and the aqueous layer extracted with EtOAc (3 x 25 mL). The combined organic layer was washed successively with sat. aq. $NaHCO_3$ (25 mL) and H_2O (25 mL), evaporated on celite and purified by dry column vacuum chromatography (4.1 x 3.3 cm) on silica gel eluting with a gradient of 0-100% CH_2Cl_2 in hexane (v/v) followed by 0.25-1.0% MeOH in CH_2Cl_2 (v/v) to give mesylate **1A** (1.303 g, 94%) as a colourless oil after coevaporation with acetonitrile (3 x 10 mL).

R_f (1% MeOH in CH_2Cl_2 (v/v)) 0.60; ^1H-NMR (300 MHz, $CDCl_3$) δ: 7.39-7.26 (15H, m), 5.02 (1H, d, *J* = 10.6 Hz), 4.92 (1H, d, *J* = 10.6 Hz), 4.84 (1H, d, *J* = 10.6 Hz), 4.80 (1H, d, *J* = 12.5 Hz), 4.66 (1H, d, *J* = 11.8 Hz), 4.63 (1H, d, *J* = 10.6 Hz), 4.60 (1H, d, *J* = 3.7 Hz), 4.41-4.32 (2H, m), 4.02 (1H, t, *J* = 9.3 Hz), 3.85 (1H, dt, *J* = 3.7, 10.0Hz), 3.52 (1H, dt, *J* = 3.7, 6.2 Hz), 3.50 (1H, bs), 3.39 (3H, s), 2.98 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 138.30, 137.75, 137.56 (C), 128.36, 128.30, 127.94, 127.84, 127.76, 127.57 (CH), 98.06, 81.73, 79.69, 76.86 (CH), 75.73, 75.09, 73.44 (CH_2), 68.59 (CH), 68.36 (CH_2), 55.46, 37.54 (CH_3). IR (cm^{-1}): 3031, 2913, 1497, 1454, 1359, 1177, 1089, 1074, 1046, 1003, 965, 931, 813, 739, 699. MALDI-MS ($C_{29}H_{34}O_8S$): $[MNa]^+$ 565.1873 (calcd. 565.1872). Anal. Calcd for $C_{29}H_{34}O_8S$: C, 64.19; H, 6.32. Found: C, 63.99; H, 6.27.



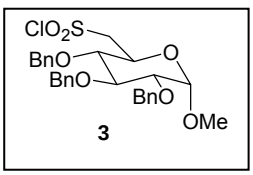
Thioacetate 2.[4,5] Mesylate **1A** (1.290 g, 2.38 mmol) was dissolved in EtOH (25 mL), KOSCMe (869 mg, 7.61 mmol) was added and the unclear solution was stirred at reflux for 4 h (orange precipitate). After cooling, 50% sat. aq. $NaHCO_3$ (100 mL) was added and the suspension was extracted with EtOAc (3 x 50 mL). The combined organic layer was washed successively with sat. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL), evaporated on celite and purified by dry column vacuum chromatography (4.1 x 3.3 cm) on silica gel eluting with a gradient of 0-30% EtOAc in hexane (v/v) to give thioacetate **2** (1.189 g, 96%) as a light orange solid.

R_f (1:1 EtOAc/hexane (v/v)) 0.64; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.41-7.32 (15H, m), 5.03 (1H, d, *J* = 10.6 Hz), 4.94 (1H, d, *J* = 10.6 Hz), 4.86 (1H, d, *J* = 10.6 Hz), 4.82 (1H, d, *J* = 11.8 Hz), 4.69 (1H, d, *J* = 11.8 Hz), 4.66 (1H, d, *J* = 10.6 Hz), 4.58 (1H, d, *J* = 3.1 Hz), 4.02 (1H, t, *J* = 9.0 Hz), 3.81 (1H, dt, *J* = 2.5, 7.5 Hz), 3.55 (1H, dd, *J* = 3.7, 9.3 Hz), 3.48 (1H, dd, *J* = 3.1, 13.7 Hz), 3.40 (3H, s), 3.35 (1H, t, *J* = 9.5 Hz), 3.08 (1H, dd, *J* = 7.5, 13.7 Hz), 2.36 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 194.67, 138.46, 137.90, 137.78 (C), 128.33, 128.29, 128.03, 127.94, 127.85, 127.81, 127.74, 127.53 (CH), 97.72, 81.69, 80.36, 79.78 (CH), 75.64, 75.04, 73.22 (CH_2), 69.23 (CH), 55.02 (CH_3), 30.73 (CH_2), 30.39 (CH_3). IR (cm^{-1}): 3063, 3031, 2908, 1694, 1497, 1454, 1358, 1201, 1156, 1136, 1092, 1072, 1050, 1029, 999, 955, 737, 698, 630. MALDI-MS ($C_{30}H_{34}O_6S$): $[MNa]^+$ 545.1974 (calcd. 545.1974). Anal. Calcd for $C_{30}H_{34}O_6S$: C, 68.94; H, 6.56. Found: C, 68.77; H, 6.63.



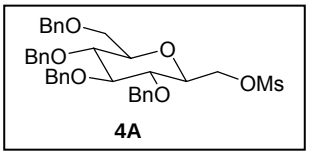
Sulfinate salt 2A.[6] Thioacetate **2** (1.180 g, 2.26 mmol) was dissolved in AcOH (25 mL), KOAc (4.082 g, 41.6 mmol) followed by Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, 4.019 g, 8.69 mmol) were added and after stirring for 15 h, sat. aq. $NaHCO_3$ (100 mL), H_2O (50 mL) and sat. aq. Na_2CO_3 (50 mL) were carefully added. After extraction with EtOAc (4 x 40 mL), the combined organic layer was washed with sat. aq. Na_2CO_3 (50 mL), evaporated on celite and purified by dry column vacuum chromatography (4.0 x 3.3 cm) on silica gel eluting with a gradient of 0-90% EtOAc in hexane (v/v) followed by 0-50% MeOH in EtOAc (v/v) to give sulfinate salt **2A** (1.116 g, 90%) as a white solid.

R_f (1:3 MeOH/EtOAc (v/v)) 0.40; ^{1}H-NMR (300 MHz, CD_3OD) δ: 7.37-7.21 (15H, m), 4.90 (1H, d, *J* = 11.2 Hz), 4.86 (1H, d, *J* = 10.6 Hz), 4.84 (1H, d, *J* = 11.2 Hz), 4.73 (1H, d, *J* = 3.1 Hz), 4.72 (1H, d, *J* = 11.2 Hz), 4.64 (1H, d, *J* = 12.5 Hz), 4.60 (1H, d, *J* = 11.2 Hz), 4.16 (1H, t, *J* = 9.2 Hz), 3.90 (1H, t, *J* = 9.3 Hz), 3.55 (1H, dd, *J* = 3.4, 9.3 Hz), 3.48 (3H, s), 3.30-3.22 (2H, m), 2.92 (1H, dd, *J* = 10.0, 14.3 Hz). ^{13}C-NMR (75 MHz, CD_3OD) δ: 140.03, 139.57, 139.55 (C), 129.42, 129.31, 129.15, 128.93, 128.89, 128.84, 128.67, 128.59 (CH), 98.53, 83.03, 81.65, 81.52 (CH), 76.44, 75.83, 73.85 (CH_2), 68.52 (CH), 55.95 (CH_3), 53.65 (CH_2). IR (cm^{-1}): 3484, 3030, 2922, 1497, 1454, 1360, 1230, 1198, 1177, 1156, 1093, 1058, 1028, 736, 696. MALDI-MS ($C_{28}H_{31}NaO_8S$): $[MNa]^+$ 573.1536 (calcd. 573.1535).



Sulfonyl chloride 3. Sulfinate salt **2A** (696 mg, 1.26 mmol) was suspended in anhydrous acetonitrile/CH_2Cl_2 (10 mL, 1:1 (v/v)) at 0°C, Ph_3P (1.002 g, 3.8 mmol) and thionyl chloride (0.40 mL, 5.5 mmol) were added sequentially and the suspension was stirred at room temperature for 13 h. EtOAc/hexane (1:4 (v/v), 100 mL) was added, the suspension was filtered through celite (4 x 15 mL EtOAc/hexane (1:3 (v/v)) washings) and the filtrate was evaporated and dried shortly under vacuum to give sulfonyl chloride **3** (657 mg, 95%) as a yellowish oil.

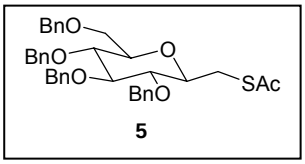
R_f (1:1 EtOAc/hexane (v/v)) 0.65; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.42-7.28 (15H, m), 5.05 (1H, d, *J* = 10.6 Hz), 4.96 (1H, d, *J* = 11.8 Hz), 4.85 (1H, d, *J* = 10.6 Hz), 4.83 (1H, d, *J* = 11.8 Hz), 4.67 (1H, d, *J* = 12.5 Hz), 4.60 (1H, d, *J* = 11.2 Hz), 4.60 (1H, d, *J* = 3.1 Hz), 4.33 (1H, t, *J* = 9.6 Hz), 4.07 (1H, t, *J* = 9.0 Hz), 3.85 (1H, dd, *J* = 1.2, 13.7 Hz), 3.55 (1H, d, *J* = 9.3 Hz), 3.52 (1H, t, *J* = 10.0 Hz), 3.46 (3H, s), 3.26 (1H, t, *J* = 9.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 138.02, 137.57, 137.06 (C), 128.58, 128.36, 128.30, 128.23, 128.12, 127.92, 127.66 (CH), 98.00, 81.56, 79.41, 78.49 (CH), 75.85, 74.76, 73.38, 66.75 (CH_2), 65.93 (CH), 55.90 (CH_3). MALDI-MS ($C_{28}H_{31}ClO_7S$): $[MNa]^+$ 569.1378 (calcd. 569.1377).



4A

Mesylate 4A.[5] Alcohol **4**[7] (1.069 g, 1.93 mmol) was dissolved in anhydrous CH_2Cl_2 (25 mL), anhydrous pyridine (3.0 mL) followed by MsCl (0.50 mL, 6.4 mmol) were added and after stirring for 2.5 h, sat. aq. $NaHCO_3$ (50 mL) was added. The layers were separated and the aqueous layer extracted with EtOAc (3 x 25 mL). The combined organic layer was washed successively with sat. aq. $NaHCO_3$ (25 mL) and H_2O (25 mL), evaporated on celite and purified by dry column vacuum chromatography (4.2 x 3.3 cm) on silica gel eluting with a gradient of 0-50% EtOAc in hexane (v/v) to give mesylate **4A** (1.202 g, 99%) as a colourless oil after coevaporation with acetonitrile (3 x 15 mL).

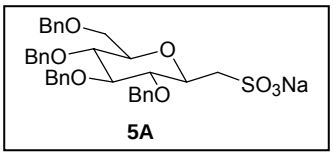
R_f (1:1 EtOAc/hexane (v/v)) 0.52; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.39-7.18 (20H, m), 4.94-4.83 (4H, m), 4.66 (1H, d, *J* = 10.9 Hz), 4.60 (1H, d, *J* = 10.9 Hz), 4.56-4.50 (3H, m), 4.37 (1H, dd, *J* = 3.7, 11.5 Hz), 3.77-3.45 (7H, m), 2.98 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 138.10, 137.70, 137.59, 137.34 (C), 128.44, 128.36, 128.33, 128.29, 127.95, 127.79, 127.75, 127.67, 127.62, 127.51 (CH), 86.76, 78.62, 77.86, 77.32, 76.86 (CH), 75.60, 75.21, 75.10, 73.36, 69.20, 68.68 (CH_2), 37.92 (CH_3). IR (cm^{-1}): 3031, 2866, 1497, 1454, 1356, 1219, 1175, 1096, 964, 914, 772, 748, 698. MALDI-MS ($C_{36}H_{40}O_8S$): $[MNa]^+$ 655.2344 (calcd. 655.2342). Anal. Calcd for $C_{36}H_{40}O_8S$: C, 68.33; H, 6.37. Found: C, 68.33; H, 6.46.



5

Thioacetate 5.[8] Mesylate **4A** (1.190 g, 1.88 mmol) was dissolved in EtOH (25 mL), KOSCMe (888 mg, 7.78 mmol) was added and the unclear solution was stirred at reflux for 16 h (orange precipitate). After cooling, 50% sat. aq. $NaHCO_3$ (100 mL) was added and the suspension was extracted with EtOAc (3 x 50 mL). The combined organic layer was washed successively with sat. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL), evaporated on celite and purified by dry column vacuum chromatography (4.0 x 3.3 cm) on silica gel eluting with a gradient of 0-40% EtOAc in hexane (v/v) to give thioacetate **5** (1.064 g, 92%) as a light orange solid.

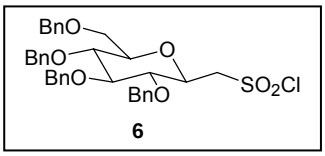
R_f (1:1 EtOAc/hexane (v/v)) 0.69; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.43-7.18 (20H, m), 4.93 (2H, s), 4.91 (1H, d, *J* = 11.8 Hz), 4.85 (1H, d, *J* = 10.6 Hz), 4.68 (1H, d, *J* = 10.6 Hz), 4.66 (1H, d, *J* = 11.8 Hz), 4.62 (1H, d, *J* = 10.0 Hz), 4.58 (1H, d, *J* = 11.8 Hz), 3.78-3.40 (8H, m), 3.10 (1H, dd, *J* = 6.2, 13.7 Hz), 2.36 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 194.82, 138.28, 138.10, 137.85, 137.60 (C), 128.35, 128.30, 128.26, 128.19, 128.13, 127.77, 127.72, 127.68, 127.62, 127.58, 127.53, 127.41 (CH), 86.85, 80.56, 79.12, 78.22, 77.86 (CH), 75.52, 75.18, 74.99, 73.42, 68.66, 31.10 (CH_2), 30.57 (CH_3). IR (cm^{-1}): 3064, 3031, 2902, 2865, 1693, 1497, 1454, 1360, 1210, 1134, 1099, 1069, 1028, 737, 698, 629. MALDI-MS ($C_{37}H_{40}O_6S$): $[MH]^+$ 613.2617 (calcd. 613.2524); $[MNa]^+$ 635.2445 (calcd. 635.2443).



5A

Sulfinate salt 5A. Thioacetate **5**(2.190 g, 3.57 mmol) was suspended in AcOH (25 mL), KOAc (4.216 g, 43 mmol) followed by Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 8.076 g, 17.5 mmol) were added and after stirring for 11 h, sat. aq. Na_2CO_3 (100 mL) and H_2O (100 mL) were carefully added. After extraction with EtOAc (5 x 100 mL), the combined organic layer was washed with sat. aq. Na_2CO_3 (50 mL), evaporated on celite and purified by dry column vacuum chromatography (4.3 x 3.3 cm) on silica gel eluting with a gradient of 0-90% EtOAc in hexane (v/v) followed by 0-50% MeOH in EtOAc (v/v) to give sulfinate salt **5A** (467 mg, 20%) as a white solid. Further extractions of the aqueous layer with CH_2Cl_2 (100 + 3 x 50 mL), evaporation on celite and purification by dry column vacuum chromatography (4.3 x 3.3 cm) on silica gel eluting with a gradient of 0-100% MeOH in EtOAc (v/v) followed by 20% MeOH in CH_2Cl_2 (v/v) gave additional sulfinate salt **5A** (810 mg, 35%) as a white solid.

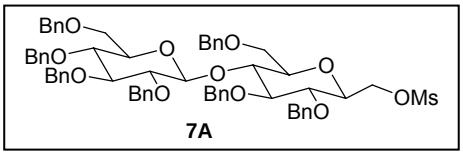
R_f (1:3 MeOH/EtOAc (v/v)) 0.49; ^{1}H-NMR (300 MHz, suspension in CD_2Cl_2/CD_3OD) δ: 7.37-7.18 (20H, m), 4.86-4.35 (8H, m), 3.86-3.21 (8H, m), 2.97 (1H, dd, *J* = 8.7, 14.3 Hz). MALDI-MS ($C_{35}H_{37}NaO_8S$): $[MH]^+$ 641.1467 (calcd. 641.2185); $[MNa]^+$ 663.1206 (calcd. 663.2005).



6

Sulfonyl chloride 6. Sulfinate salt **5A** (810 mg, 1.26 mmol) was suspended in anhydrous acetonitrile/CH_2Cl_2 (30 mL, 2:1 (v/v)) at 0°C, Ph_3P (2.087 g, 7.96 mmol) and thionyl chloride (1.50 mL, 21 mmol) were added sequentially at 0°C and the suspension was stirred at room temperature for 2.5 h. EtOAc/hexane (1:4 (v/v), 100 mL) was added, the suspension was filtered through celite (2 x 12.5 mL EtOAc/hexane (1:4 (v/v)) washings) and the filtrate was evaporated and dried shortly under vacuum to give sulfonyl chloride **6** (871 mg, quant.) as a light yellow oil.

R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.84; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.48-7.21 (20H, m), 5.02-4.85 (4H, m), 4.68-4.55 (4H, m), 3.98-3.35 (9H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 137.86, 137.72, 137.68, 136.96 (C), 128.64, 128.34, 128.32, 128.27, 128.24, 128.20, 127.99, 127.79, 127.67, 127.61, 127.49 (CH), 86.83, 79.20, 78.46, 77.59 (CH), 75.68, 74.96, 74.82 (CH_2), 74.20 (CH), 73.46, 68.04, 66.69 (CH_2). MALDI-MS ($C_{35}H_{37}ClO_7S$): $[MNa]^+$ 659.1849 (calcd. 659.1846).

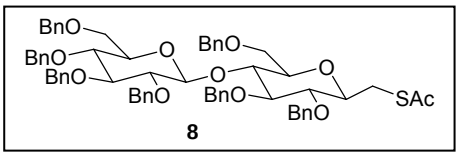


7A

Mesylate 7A. Alcohol **7**[9] (895.3 mg, 0.907 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL), anhydrous pyridine (1.0 mL) followed by MsCl (0.20 mL, 2.6 mmol) were added and after stirring for 1 h, sat. aq. $NaHCO_3$ (40 mL) was added. The layers were separated and the aqueous layer extracted with EtOAc (3 x 20 mL). The combined organic layer was washed successively with sat. aq. $NaHCO_3$ (20 mL) and H_2O (20 mL), evaporated on celite and purified by dry column vacuum chromatography (4.2 x 3.3 cm) on silica gel eluting with a gradient of 0-50% EtOAc in hexane (v/v) to give mesylate **7A** (830.7 mg, 86%) as a white solid.

R_f (1:1 EtOAc/hexane (v/v)) 0.67; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.49-7.24 (35H, m), 5.31 (1H, d, *J* = 11.2 Hz), 5.00 (1H, d, *J* = 11.2 Hz), 4.98-4.79 (6H, m), 4.66-4.36 (9H, m), 4.09 (1H, t, *J* = 9.3 Hz), 3.90 (1H, dd, *J* = 2.8, 10.9 Hz), 3.83 (1H, d, *J* = 10.0 Hz), 3.75-3.62 (5H, m), 3.55-3.39 (5H, m), 2.97 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 138.97, 138.37, 138.21, 138.04, 137.61 (C), 128.37, 128.29, 128.18, 128.08, 127.93, 127.84, 127.76, 127.38, 127.34, 127.24, 102.51, 84.86, 82.64, 78.70, 77.94, 76.84, 76.53, 76.38, 75.57 (CH), 75.22, 75.09 (CH_2), 74.96, 74.78 (CH_2, CH), 73.21, 73.02, 69.22, 68.89, 67.76 (CH_2), 37.74 (CH_3). IR (cm^{-1}): 3063, 3030, 2867, 1497, 1454, 1358,

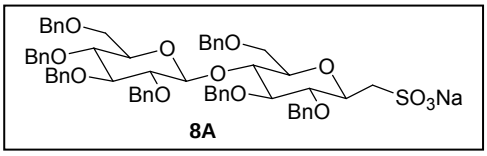
1277, 1209, 1174, 1150, 1092, 1071, 1028, 984, 922, 812, 737, 698, 527. MALDI-MS ($C_{63}H_{68}O_{13}S$): $[MNa]^+$ 1087.4284 (calcd. 1087.4278). Anal. Calcd for $C_{63}H_{68}O_{13}S$: C, 71.03; H, 6.43. Found: C, 70.94; H, 6.62.



8

Thioacetate 8. Mesylate **7A** (825 mg, 0.774 mmol) was dissolved in EtOH (20 mL), KOSCMe (278 mg, 2.43 mmol), *i*PrOH (10 mL) and THF (10 mL) were added and the orange solution was stirred at reflux for 3 h (orange precipitate). Additional KOSCMe (512 mg, 4.48 mmol) was added and the suspension was stirred at reflux for 16 h. After cooling, 50% sat. aq. $NaHCO_3$ (100 mL) was added and the suspension was extracted with ether (4 x 30 mL). The combined organic layer was washed successively with sat. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL), evaporated on celite and purified by dry column vacuum chromatography (4.2 x 3.3 cm) on silica gel eluting with a gradient of 0-50% EtOAc in hexane (v/v) to give thioacetate **8** (637 mg, 79%) as a light orange solid.

R_f (1:3 EtOAc/hexane (v/v)) 0.45; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.43-7.19 (35H, m), 5.22 (1H, d, *J* = 11.2 Hz), 4.92 (1H, d, *J* = 11.2 Hz), 4.88 (1H, d, *J* = 11.2 Hz), 4.87-4.71 (5H, m), 4.62 (1H, d, *J* = 12.5 Hz), 4.60-4.43 (5H, m), 4.41 (1H, d, *J* = 11.8 Hz), 4.06 (1H, t, *J* = 9.3 Hz), 3.86 (1H, dd, *J* = 3.7, 11.2 Hz), 3.75 (1H, dd, *J* = 1.6, 10.9 Hz), 3.69-3.55 (5H, m), 3.51-3.31 (6H, m), 3.05 (1H, dd, *J* = 6.8, 13.7 Hz), 2.34 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 195.04, 139.19, 138.53, 138.30, 138.24, 138.17, 137.96 (C), 128.33, 128.26, 128.20, 128.04, 127.79, 127.71, 127.63, 127.55, 127.47, 127.29, 127.19, 102.40, 85.12, 84.88, 82.71, 79.85, 79.30, 78.05, 77.87 (CH), 75.62, 75.18 (CH_2), 75.09 (CH), 74.94, 74.81, 73.26, 73.21, 68.96, 67.86, 31.12 (CH_2), 30.49 (CH_3). IR (cm^{-1}): 3030, 2868, 1692, 1496, 1454, 1358, 1210, 1067, 1028, 773, 735, 698, 626. MALDI-MS ($C_{64}H_{68}O_{11}S$): $[MNa]^+$ 1067.4365 (calcd. 1067.4380). Anal. Calcd for $C_{64}H_{68}O_{11}S$: C, 73.54; H, 6.56. Found: C, 73.50; H, 6.60.

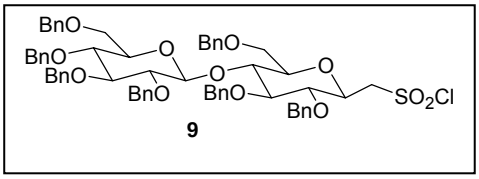


8A

Sulfinate salt 8A. Thioacetate **8** (631 mg, 0.604 mmol) was suspended in AcOH (10 mL), KOAc (933 mg, 9.5 mmol) followed by Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 1.179 g, 2.55 mmol) were added and after stirring for 18 h, sat. aq. Na_2CO_3 (50 mL) and H_2O (50 mL) were carefully added. After extraction with $CHCl_3$ (4 x 25 mL), the combined organic layer was washed with sat. aq. Na_2CO_3 (25 mL), evaporated on celite and purified by dry column vacuum chromatography (4.1 x 3.3 cm) on silica gel eluting with a gradient of 0-20% MeOH in CH_2Cl_2 (v/v) to give sulfinate salt **8A** (622 mg, 96%) as a colourless oil.

R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.29; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.40-7.14 (35H, m), 5.19-4.34 (15H, m), 4.17-3.22 (15H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 138.97, 138.32, 138.21, 138.06, 137.88, 137.84, 128.70, 128.36, 128.18, 128.05, 127.86, 127.76, 127.63, 127.57, 127.44, 127.29, 127.20, 126.94, 84.53, 84.45, 82.01, 79.48, 77.96, 77.75, 76.06, 76.01, 75.46, 74.94, 74.79, 74.67, 74.57, 73.28, 73.08, 73.02, 53.42. IR (cm^{-1}): 3478, 3063, 3030, 2870, 1497, 1454, 1361, 1315, 1210, 1174, 1069, 1048, 1028, 736, 698, 621. MALDI-MS ($C_{62}H_{65}NaO_{13}S$): $[MH]^+$ 1073.4098 (calcd. 1073.4122); $[MNa]^+$ 1095.3926 (calcd. 1095.3941).

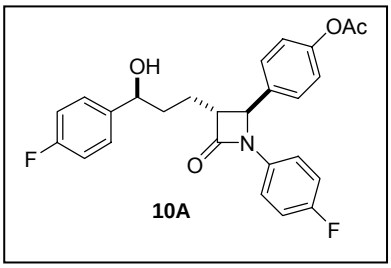
Sulfonyl chloride 9. Sulfinate salt **8A** (334 mg, 0.311 mmol) was dissolved in anhydrous acetonitrile/CH_2Cl_2 (4 mL, 1:1 (v/v)) at 0°C, Ph_3P (264 mg, 1.01 mmol) and thionyl chloride (0.10 mL, 1.37 mmol) were added sequentially at 0°C and the suspension was stirred at room



9

temperature for 6 h. EtOAc/hexane (1:4 (v/v), 30 mL) was added, the suspension was filtered through a short pad of silica gel (4 x 5 mL EtOAc/hexane (1:3 (v/v)) washings) and the filtrate was evaporated and dried shortly under vacuum to give sulfonyl chloride **9** (220 mg, 66%) as a light yellow foam.

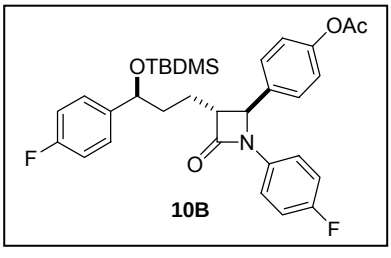
R_f (1:3 EtOAc/hexane (v/v)) 0.38; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.50-7.26 (35H, m), 5.30 (1H, d, *J* = 11.2 Hz), 4.98 (1H, d, *J* = 10.6 Hz), 4.96-4.81 (5H, m), 4.79 (1H, d, *J* = 10.6 Hz), 4.67-4.50 (6H, m), 4.48 (1H, d, *J* = 11.8 Hz), 4.23-4.15 (1H, m), 3.98-3.91 (2H, m), 3.85-3.57 (8H, m), 3.51-3.38 (3H, m), 3.30 (1H, t *J* = 9.0 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 138.77, 138.45, 138.17, 138.11, 137.78, 137.27 (C), 128.63, 128.38, 128.31, 128.18, 128.12, 127.94, 127.78, 127.70, 127.63, 127.55, 127.42, 127.29, 102.32, 84.98, 84.80, 82.66, 79.23, 77.95, 77.82, 75.78 (CH), 75.60, 75.38 (CH_2), 75.12 (CH), 74.99, 74.78, 74.70 (CH_2), 74.21 (CH), 73.24, 68.95, 67.35, 66.79 (CH_2). IR (cm^{-1}): 3089, 3063, 3030, 2868, 1496, 1454, 1362, 1313, 1280, 1209, 1167, 1091, 1067, 1028, 913, 771, 736, 698, 601. MALDI-MS ($C_{62}H_{65}ClO_{12}S$): $[MNa]^+$ 1091.3767 (calcd. 1091.3783).



10A

Acetate 10A.[10] Ezetimibe **10**[11] (5.530 g, 13.5 mmol) was suspended in 2-propanol (70 mL), aq. NaOH (2M, 15 mL) followed by Ac_2O (3.0 mL, 32 mmol) were added and the solution was stirred for 5 h followed by addition of sat. aq. $NaHCO_3$ (200 mL). After extraction with EtOAc (4 x 50 mL), the combined organic layer was washed with sat. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL), evaporated on celite and purified by dry column vacuum chromatography (5.2 x 5.5 cm) on silica gel eluting with a gradient of 0-100% EtOAc in hexane (v/v) to give acetate **10A** (5.930 g, 97%) as a white foam.

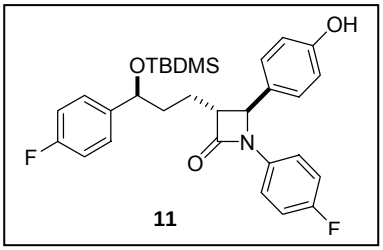
R_f (1:1 EtOAc/hexane (v/v)) 0.35; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.31 (2H, d, *J* = 8.7 Hz), 7.29-7.18 (4H, m), 7.09 (2H, d, *J* = 8.7 Hz), 6.99 (2H, t, *J* = 8.7 Hz), 6.92 (2H, t, *J* = 8.7 Hz), 4.67 (1H, bs), 4.61 (1H, d, *J* = 2.5 Hz), 3.08-3.04 (1H, m), 2.75 (1H, bs), 2.29 (3H, s), 1.97-1.85 (4H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 169.16, 167.23, 163.56, 160.46, 160.32, 157.24, 150.58, 139.94, 139.90, 134.85, 133.53, 133.50 (C), 127.32, 127.21, 126.78, 122.38, 118.34, 118.23, 115.95, 115.65, 115.35, 115.07 (CH), 72.95, 60.81, 60.33 (CH), 36.61, 25.07 (CH_2), 21.19 (CH_3). IR (cm^{-1}): 3443, 3019, 2936, 2862, 1747, 1605, 1509, 1427, 1388, 1370, 1221, 1198, 1157, 1016, 835, 757, 668. MALDI-MS ($C_{26}H_{23}F_2NO_4$): $[MH\text{-}H_2O]^+$ 434.1556 (calcd. 434.1568); $[MNa]^+$ 474.1485 (calcd. 474.1493).



10B

Silyl ether 10B.[10] Acetate **10A** (1.864 g, 4.13 mmol) was dissolved in anhydrous DMF (25 mL), imidazole (939 mg, 13.8 mmol) and TBDMSCl (1.853 g, 12.3 mmol) were added sequentially and the solution was stirred for 3 h followed by addition of 50% sat. aq. $NaHCO_3$ (150 mL). After extraction with EtOAc (4 x 40 mL), the combined organic layer was washed successively with sat. aq. $NaHCO_3$ (40 mL) and H_2O (40 mL), evaporated on celite and purified by dry column vacuum chromatography (4.2 x 5.5 cm) on silica gel eluting with a gradient of 0-30% EtOAc in hexane (v/v) to give silyl ether **10B** (2.137 g, 91%) as a colourless oil.

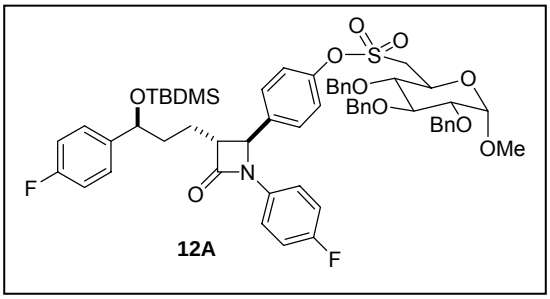
R_f (1:1 EtOAc/hexane (v/v)) 0.69; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.31 (2H, d, *J* = 8.7 Hz), 7.26-7.20 (4H, m), 7.10 (2H, d, *J* = 8.7 Hz), 6.98 (2H, t, *J* = 8.7 Hz), 6.91 (2H, t, *J* = 8.7 Hz), 4.67 (1H, t, *J* = 5.3 Hz), 4.58 (1H, d, *J* = 1.9 Hz), 3.06-3.02 (1H, m), 2.28 (3H, s), 1.96-1.80 (4H, m), 0.88 (9H, s), 0.02 (3H, s), -0.16 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 169.16, 167.06, 163.42, 160.47, 160.16, 157.23, 150.62, 140.50, 135.10, 133.74, 133.70 (C), 127.26, 127.14, 126.77, 122.37, 118.27, 118.16, 115.89, 115.58, 115.03, 114.76 (CH), 73.74, 60.67, 60.53 (CH), 37.94 (CH_2), 25.73 (CH_3), 24.55 (CH_2), 20.99 (CH_3), 18.07 (C), -4.74, -5.05 (CH_3). IR (cm^{-1}): 2953, 2930, 2857, 1752, 1606, 1510, 1472, 1426, 1385, 1370, 1252, 1219, 1197, 1166, 1140, 1102, 1086, 1015, 912, 835, 777, 736. MALDI-MS ($C_{32}H_{37}F_2NO_4Si$): $[MH\text{-}TBDMSOH]^+$ 434.1556 (calcd. 434.1568); $[MNa]^+$ 588.2347 (calcd. 588.2358). Anal. Calcd for $C_{32}H_{37}F_2NO_4Si$: C, 67.94; H, 6.59; N, 2.48. Found: C, 67.94; H, 6.64; N, 2.37.



11

Phenol 11.[10] Silyl ether **10B** (5.123 g, 9.06 mmol) was dissolved in CH_2Cl_2 (200 mL), neutral alumina (50 g) was added and the suspension was evaporated to dryness. The coated alumina was dried shortly under vacuum and then heated to 70°C for 5.5 h. After cooling, the alumina was extracted with 10% MeOH in CH_2Cl_2 (8 x 50 mL) and the combined organic extracts were evaporated on celite and purified by dry column vacuum chromatography (5.4 x 5.5 cm) on silica gel eluting with a gradient of 0-30% EtOAc in hexane (v/v) to give phenol **11** (3.919 g, 83%) as a white foam.

R_f (1:3 EtOAc/hexane (v/v)) 0.24; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.26-7.14 (6H, m), 6.99-6.83 (6H, m), 6.16 (1H, bs), 4.65 (1H, t, *J* = 5.3 Hz), 4.52 (1H, d, *J* = 1.9 Hz), 3.04-2.98 (1H, m), 1.92-1.76 (4H, m), 0.86 (9H, s), 0.00 (3H, s), -0.17 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 167.82, 163.28, 160.42, 156.12, 140.50, 140.45, 133.57 (C), 128.92, 127.19, 127.15, 127.08, 118.43, 118.32, 116.05, 115.85, 115.55, 115.01, 114.72 (CH), 73.82, 61.17, 60.35 (CH), 38.07 (CH_2), 25.89 (CH_3), 24.68 (CH_2), 18.25 (C), -4.54, -4.84 (CH_3). IR (cm^{-1}): 3351, 2953, 2938, 2857, 1722, 1615, 1604, 1510, 1450, 1391, 1361, 1252, 1223, 1156, 1103, 1087, 863, 834, 776, 760. MALDI-MS ($C_{30}H_{35}F_2NO_3Si$): $[MH\text{-}TBDMSOH]^+$ 392.1451 (calcd. 392.1462); $[MH]^+$ 524.2409 (calcd. 524.2433); $[MNa]^+$ 546.2242 (calcd. 546.2252). Anal. Calcd for $C_{30}H_{35}F_2NO_3Si$: C, 68.81; H, 6.74; N, 2.67. Found: C, 68.61; H, 6.82; N, 2.66.

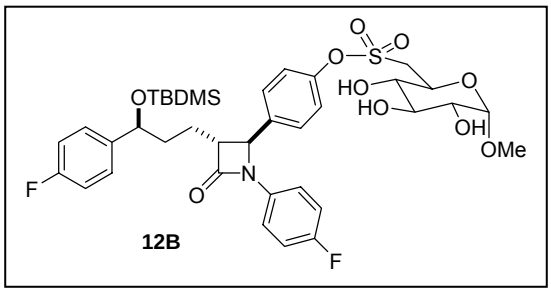


12A

Sulfonate 12A. Sulfonyl chloride **3** (197 mg, 0.36 mmol) was suspended in anhydrous CH_2Cl_2 (5 mL), anhydrous pyridine (0.5 mL) followed by phenol **11** (70.0 mg, 0.13 mmol) were added and the solution was stirred for 22 h, diluted with EtOAc (25 mL) and washed sequentially with sat. aq. $NaHCO_3$ (10 mL) and H_2O (10 mL). The organic layer was evaporated on celite and purified by dry column vacuum chromatography (4.3 x 2.0 cm) on silica gel eluting with a gradient of 0-35% EtOAc in hexane (v/v) to give sulfonate **12A** (125.5 mg, 91%) as a colourless oil/glass.

R_f (1% MeOH in CH_2Cl_2 (v/v)) 0.77; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.37-7.14 (23H, m), 7.00 (2H, t, *J* = 8.7 Hz), 6.95 (2H, t, *J* = 8.7 Hz), 5.05 (1H, d, *J* = 11.2 Hz), 4.97 (1H, d, *J* = 11.2 Hz), 4.84 (1H, d, *J* = 11.8 Hz), 4.82 (1H, d, *J* = 10.6 Hz), 4.69 (1H, t, *J* = 6.8 Hz), 4.67 (1H, d, *J* = 12.5 Hz), 4.60

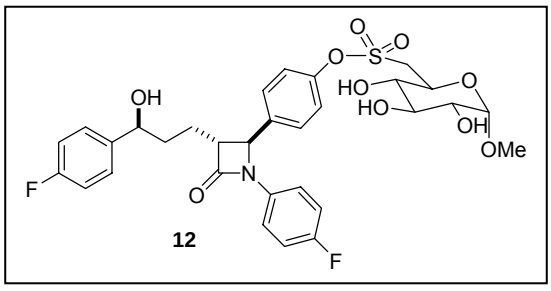
(1H, d, *J* = 3.7 Hz), 4.56 (1H, d, *J* = 12.5 Hz), 4.54 (1H, d, *J* = 10.6 Hz), 4.29 (1H, t, *J* = 9.5 Hz), 4.06 (1H, t, *J* = 9.0 Hz), 3.57 (1H, t, *J* = 3.1 Hz), 3.53 (1H, d, *J* = 3.1 Hz), 3.46 (3H, s), 3.26 (1H, t, *J* = 9.3 Hz), 3.14 (1H, dd, *J* = 10.0, 14.3 Hz), 2.96 (1H, dt, *J* = 1.9, 6.8 Hz), 1.97-1.78 (4H, m), 0.90 (9H, s), 0.04 (3H, s), -0.13 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 166.62, 163.27, 160.37, 160.03, 157.14, 148.91, 140.33, 138.05, 137.63, 137.29, 136.67, 133.45, 133.42 (C), 128.44, 128.31, 128.18, 128.04, 127.96, 127.86, 127.65, 127.15, 127.03, 126.97, 123.15, 118.13, 118.03, 115.93, 115.64, 115.02, 114.75 (CH), 97.92, 81.67, 79.60, 79.23 (CH), 75.78, 74.86 (CH_2), 73.78 (CH), 73.37 (CH_2), 65.64, 60.66, 60.48 (CH), 55.73 (CH_3), 51.63, 38.06 (CH_2), 25.85 (CH_3), 24.69 (CH_2), 18.22 (C), -4.54, -4.87 (CH_3). IR (cm^{-1}): 3032, 2930, 2858, 1750, 1605, 1510, 1455, 1386, 1252, 1220, 1153, 1086, 1073, 1048, 870, 836, 755, 699. MALDI-MS ($C_{58}H_{65}F_2NO_{10}SiS$): $[MNa]^+$ 1056.3969 (calcd. 1056.3964). Anal. Calcd for $C_{58}H_{65}F_2NO_{10}SiS$: C, 67.35; H, 6.33; N, 1.35. Found: C, 67.43; H, 6.44; N, 1.33.



12B

β-Lactam 12B. Sulfonate **12A** (105.1 mg, 0.102 mmol) was dissolved in EtOH (5 mL), $Pd(OH)_2/C$ (20% (w/w), 33 mg) was added and the suspension was evacuated 4 times with H_2 and stirred under an H_2-atmosphere for 6 h. The suspension was evaporated on celite and purified by dry column vacuum chromatography (4.2 x 2.0 cm) on silica gel eluting with a gradient of 0-10% MeOH in CH_2Cl_2 (v/v) to give β-lactam **12B** (63.2 mg, 81%) as a colourless oil.

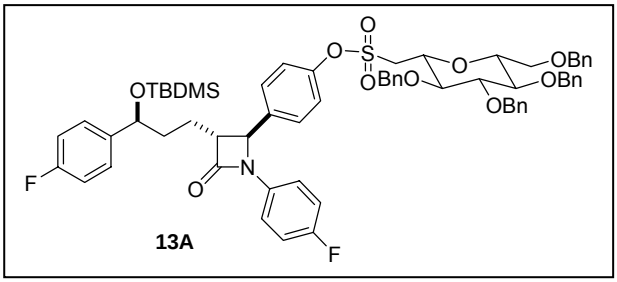
R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.36; ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.55 (2H, d, *J* = 8.7 Hz), 7.42 (2H, d, *J* = 8.7 Hz), 7.37 (2H, dd, *J* = 5.9, 8.4 Hz), 7.28 (2H, dd, *J* = 5.0, 9.3 Hz), 7.11-7.01 (4H, m), 4.96 (1H, d, *J* = 1.9 Hz), 4.84 (1H, t, *J*= 5.3 Hz), 4.69 (1H, d, *J* = 3.7 Hz), 4.61 (1H, d, *J* = 5.0 Hz), 4.35 (1H, d, *J* = 3.1 Hz), 4.16 (1H, dt, *J* = 1.2, 10.0 Hz), 3.87 (1H, dd, *J* = 1.2, 14.9 Hz), 3.79 (1H, d, *J* = 7.5 Hz), 3.65 (1H, t, *J* = 9.0 Hz), 3.56 (1H, dd, *J* = 10.0, 14.9 Hz), 3.45-3.40 (1H, m), 3.38 (3H, s), 3.27-3.14 (2H, m), 2.00-1.88 (4H, m), 0.87 (9H, s), 0.05 (3H, s), -0.15 (3H, s). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 167.25, 163.96, 160.84, 160.75, 157.65, 150.14, 141.91, 141.87, 138.13, 134.95, 134.91 (C), 128.32, 128.23, 123.84, 118.98, 118.88, 116.43, 116.12, 115.49, 115.21 (CH), 100.74, 74.77, 74.42, 73.55, 73.04, 68.01, 61.25, 60.50 (CH), 55.56 (CH_3), 52.83, 38.50 (CH_2), 26.16 (CH_3), 25.34 (CH_2), 18.65 (C), -4.47, -4.71 (CH_3). IR (cm^{-1}): 3396, 2951, 2931, 2857, 1754, 1701, 1605, 1510, 1426, 1385, 1250, 1220, 1151, 1103, 1088, 1053, 1015, 988, 872, 836, 778. MALDI-MS ($C_{37}H_{47}F_2NO_{10}SSi$): $[MNa]^+$ 786.2559 (calcd. 786.2556).



12

β-Lactam 12. β-Lactam **12B** (58.9 mg, 0.077 mmol) was dissolved in anhydrous THF (2.5 mL, teflon bottle), anhydrous pyridine (0.5 mL) followed by HF·pyridine complex (0.5 mL) were added and the solution was stirred for 14.5 h, diluted with ether (20 mL) and washed with sat. aq. $NaHCO_3$ (3 x 5 mL). The organic layer was evaporated on celite and purified by dry column vacuum chromatography (4.2 x 2.0 cm) on silica gel eluting with a gradient of 0-10% MeOH in CH_2Cl_2 (v/v) to give β-lactam **12** (44.9 mg, 90%) as a white solid.

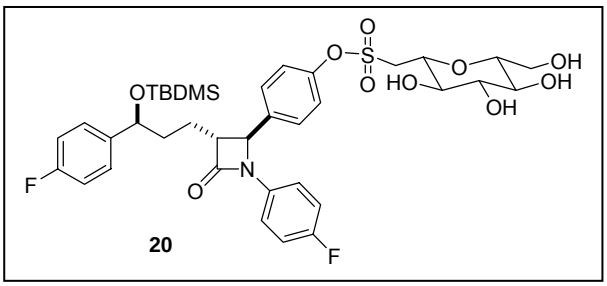
R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.26; ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.56 (2H, d, *J* = 8.7 Hz), 7.43 (2H, d, *J* = 8.7 Hz), 7.37 (2H, dd, *J* = 5.6, 8.7 Hz), 7.30 (2H, dd, *J* = 4.7, 9.0 Hz), 7.06 (2H, d, *J* = 9.3 Hz), 7.03 (2H, d, *J* = 8.7 Hz), 4.99 (1H, d, *J* = 2.5 Hz), 4.69 (1H, d, *J* = 3.7 Hz), 4.61 (1H, d, *J*= 5.0 Hz), 4.42 (1H, d, *J* = 3.7 Hz), 4.34 (1H, bs), 4.15 (1H, dt, *J* = 1.2, 8.7 Hz), 3.86 (1H, dd, *J* = 1.2, 14.9 Hz), 3.79 (1H, d, *J* = 8.1 Hz), 3.65 (1H, t, *J* = 8.7 Hz), 3.57 (1H, dd, *J* = 10.0, 14.9 Hz), 3.44-3.38 (1H, m), 3.38 (3H, s), 3.32-3.14 (2H, m), 2.08-1.86 (4H, m). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 167.42, 163.87, 160.85, 157.67, 150.13, 142.52, 138.18, 134.93 (C), 128.35, 128.22, 128.13, 123.83, 119.01, 118.89, 116.44, 116.13, 115.40, 115.11 (CH), 100.74, 74.77, 73.56, 73.04, 72.77, 68.01, 61.27, 60.56 (CH), 55.56 (CH_3), 52.83, 37.54, 25.70 (CH_2). IR (cm^{-1}): 3395, 2925, 1732, 1604, 1509, 1365, 1219, 1148, 1103, 1051, 1014, 871, 834, 752. MALDI-MS ($C_{31}H_{33}F_2NO_{10}S$): $[MNa]^+$ 672.1693 (calcd. 672.1691). Anal. Calcd for $C_{31}H_{33}F_2NO_{10}S$: C, 57.31; H, 5.12; N, 2.16. Found: C, 57.34; H, 5.26; N, 2.21.



13A

Sulfonate 13A. Sulfonyl chloride **6** (871 mg, 1.26 mmol) was suspended in anhydrous CH_2Cl_2 (10 mL), anhydrous pyridine (1.0 mL) followed by phenol **11** (334 mg, 0.634 mmol) were added and the solution was stirred for 13 h, diluted with EtOAc (50 mL) and washed sequentially with sat. aq. $NaHCO_3$ (20 mL) and H_2O (20 mL). The organic layer was evaporated on celite and purified by dry column vacuum chromatography (4.3 x 3.3 cm) on silica gel eluting with a gradient of 0-100% CH_2Cl_2 in hexane (v/v) to give sulfonate **13A** (657 mg, 92%) as a white foam.

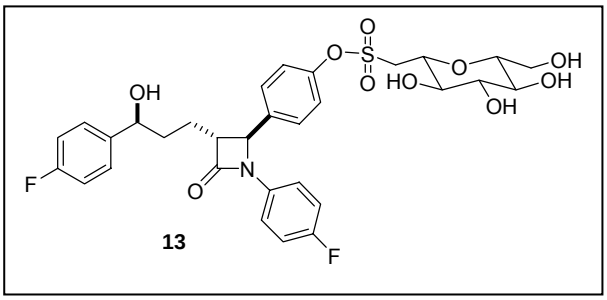
R_f (1:1 EtOAc/hexane (v/v)) 0.76; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.37-7.15 (28H, m), 7.01 (2H, t, *J* = 8.7 Hz), 6.96 (2H, t, *J* = 8.7 Hz), 5.03-4.81 (4H, m), 4.73-4.51 (6H, m), 3.95 (1H, t, *J* = 8.4 Hz), 3.78 (4H, bs), 3.57-3.53 (1H, m), 3.48 (1H, d, *J* = 1.2 Hz), 3.40 (1H, t, *J* = 9.0 Hz), 3.24 (1H, dd, *J* = 9.3, 14.9 Hz), 3.02-2.95 (1H, m), 1.97-1.80 (4H, m), 0.92 (9H, s), 0.06 (3H, s), -0.11 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 166.72, 163.24, 160.35, 160.01, 157.13, 149.25, 140.37, 140.33, 137.90, 137.65, 137.58, 137.12, 136.97, 136.52, 133.52, 133.48 (C), 128.46, 128.32, 128.28, 128.17, 128.02, 127.97, 127.81, 127.76, 127.67, 127.63, 127.52, 127.13, 127.02, 123.32, 118.13, 118.02, 115.90, 115.60, 115.01, 114.72 (CH), 86.83, 79.13, 78.83, 77.73 (CH), 75.56, 75.00, 74.85 (CH_2), 74.19, 73.77 (CH), 73.31 (CH_2), 68.36, 60.57, 60.53 (CH), 51.31, 38.03 (CH_2), 25.85 (CH_3), 24.67 (CH_2), 18.20 (C), -4.57, -4.87 (CH_3). IR (cm^{-1}): 2951, 2929, 2858, 1751, 1605, 1510, 1454, 1386, 1362, 1251, 1220, 1151, 1102, 871, 835, 776, 754, 699. MALDI-MS ($C_{65}H_{71}F_2NO_{10}SiS$): $[MNa]^+$ 1146.4440 (calcd. 1146.4434). Anal. Calcd for $C_{65}H_{71}F_2NO_{10}SiS$: C, 69.43; H, 6.36; N, 1.25. Found: C, 69.27; H, 6.47; N, 1.28.



20

β-Lactam 20. Sulfonate **13A** (236 mg, 0.210 mmol) was dissolved in EtOH/EtOAc (10 mL, 1:1 (v/v)), $Pd(OH)_2/C$ (20% (w/w), 73 mg) was added and the suspension was evacuated 4 times with H_2 and stirred under an H_2-atmosphere for 3.5 h. The suspension was evaporated on celite and purified by dry column vacuum chromatography (4.6 x 2.0 cm) on silica gel eluting with a gradient of 0-20% MeOH in CH_2Cl_2 (v/v) to give β-lactam **20** (145 mg, 90%) as a white foam.

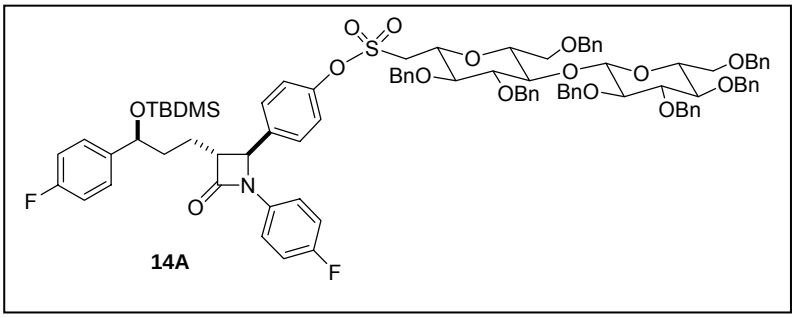
R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.25; ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.55 (2H, dd, *J* = 6.5, 8.7 Hz), 7.47 (2H, d, *J* = 8.4 Hz), 7.40-7.20 (4H, m), 7.11-6.98 (4H, m), 4.97 (1H, dd, *J* = 2.3, 10.5 Hz), 4.83 (1H, bs), 4.61 (1H, bs), 4.48 (1H, bs), 4.30 (1H, bs), 3.90-3.81 (3H, m), 3.71-3.64 (1H, m), 3.56-3.38 (5H, m), 3.25-3.14 (2H, m), 2.66 (1H, t, *J* = 7.2 Hz), 1.98-1.81 (4H, m), 0.88 (9H, s), 0.05 (3H, s), -0.15 (3H, s). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 168.30, 161.88, 158.69, 151.25, 142.96, 139.63, 139.16, 139.13, 135.98 (C), 131.66, 131.56, 129.36, 129.28, 124.92, 120.00, 119.90, 117.46, 117.16, 116.62, 116.52 (CH), 82.13, 80.16, 76.75, 75.44, 74.46, 72.35 (CH), 63.64 (CH_2), 61.60, 61.55 (CH), 54.03, 39.52 (CH_2), 27.20 (CH_3), 26.35 (CH_2), 19.68 (C), -3.44, -3.69 (CH_3). IR (cm^{-1}): 3380, 2930, 2858, 1749, 1604, 1510, 1385, 1363, 1220, 1172, 1149, 1088, 1032, 1016, 872, 835, 757. MALDI-MS ($C_{37}H_{47}F_2NO_{10}SiS$): $[MNa]^+$ 786.2563 (calcd. 786.2556). Anal. Calcd for $C_{37}H_{47}F_2NO_{10}SiS$: C, 58.17; H, 6.20; N, 1.83. Found: C, 58.02; H, 6.26; N, 1.85.



13

β-Lactam 13. β-Lactam **21** (31.5 mg, 0.041 mmol) was dissolved in anhydrous THF (2.5 mL, teflon bottle), anhydrous pyridine (0.5 mL) followed by HF·pyridine complex (0.5 mL) were added and the solution was stirred for 24 h, diluted with ether (20 mL) and washed with sat. aq. $NaHCO_3$ (3 x 5 mL). The organic layer was evaporated on celite and purified by dry column vacuum chromatography (4.3 x 2.0 cm) on silica gel eluting with a gradient of 0-20% MeOH in CH_2Cl_2 (v/v) to give β-lactam **13** (9.8 mg, 37%) as a white solid.

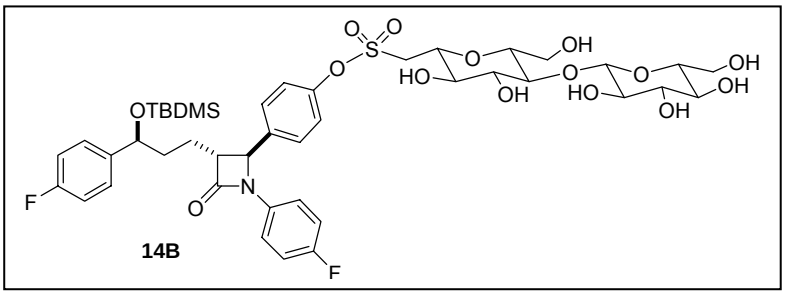
R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.22 (run twice); ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.55 (2H, d, *J* = 8.7 Hz), 7.47 (2H, d, *J* = 8.7 Hz), 7.36 (2H, dd, *J* = 5.6, 8.7 Hz), 7.29 (2H, dd, *J* = 4.8, 9.2 Hz), 7.06 (2H, d, *J* = 8.7 Hz), 7.03 (2H, d, *J* = 9.0 Hz), 4.98 (1H, d, *J* = 2.5 Hz), 4.68 (1H, bs), 4.58 (1H, bs), 4.38 (1H, bs), 4.27 (1H, bs), 3.89-3.80 (3H, m), 3.66 (1H, d, *J* = 10.6 Hz), 3.54-3.36 (5H, m), 3.24-3.14 (2H, m), 2.00-1.86 (4H, m). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 168.48, 151.29, 143.63, 139.23, 136.09 (C), 129.37, 129.29, 129.19, 124.97, 120.05, 119.94, 117.49, 117.18, 116.46, 116.18 (CH), 82.17, 80.18, 76.78, 74.49, 73.79, 72.42 (CH), 63.67 (CH_2), 62.35, 61.63 (CH), 54.06, 38.62, 26.75 (CH_2). IR (cm^{-1}): 3364, 2924, 1734, 1509, 1388, 1220, 1148, 1102, 872, 835, 769. MALDI-MS ($C_{31}H_{33}F_2NO_{10}S$): $[MNa]^+$ 672.1744 (calcd. 672.1691).



14A

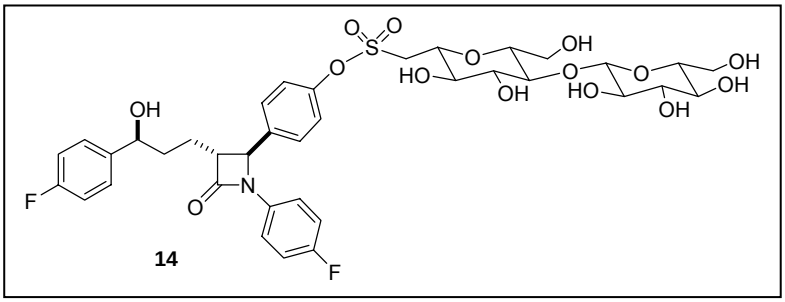
Sulfonate 14A. Sulfonyl chloride **9** (271 mg, 0.253 mmol) was dissolved in anhydrous CH_2Cl_2 (3 mL), anhydrous pyridine (0.5 mL) followed by phenol **11** (75.7 mg, 0.145 mmol) were added and the solution was stirred for 38 h, diluted with EtOAc (50 mL) and washed sequentially with sat. aq. $NaHCO_3$ (15 mL) and H_2O (15 mL). The organic layer was evaporated on celite and purified by dry column vacuum chromatography (4.5 x 3.3 cm) on silica gel eluting with a gradient of 0-20% EtOAc in toluene (v/v) to give a 4:1 mixture of sulfonate **14A** and unreacted phenol **11** (166 mg) as a white foam.

R_f (1:1 EtOAc/hexane (v/v)) 0.73; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.49-7.17 (41H, m), 7.06 (2H, d, *J* = 8.7 Hz), 7.02 (2H, t, *J* = 8.1 Hz), 6.96 (2H, d, *J* = 8.7 Hz), 5.31 (1H, d, *J* = 11.2 Hz), 5.01-4.74 (7H, m), 4.65-4.45 (8H, m), 4.21 (1H, t, *J* = 9.3 Hz), 4.02-3.96 (2H, m), 3.86-3.60 (6H, m), 3.53-3.47 (4H, m), 3.33 (1H, d, *J* = 9.3 Hz), 3.26 (1H, t, *J* = 9.0 Hz), 3.19 (1H, d, *J* = 9.3 Hz), 3.06-3.00 (1H, m), 2.06-1.84 (4H, m), 0.96 (9H, s), 0.10 (3H, s), -0.07 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 166.70, 160.35, 160.00, 156.27, 149.33, 140.35, 140.31, 138.63, 138.26, 138.00, 137.90, 137.59, 137.45, 137.29, 136.51, 133.47 (C), 128.82, 128.73, 128.34, 128.19, 128.08, 127.98, 127.85, 127.66, 127.56, 127.45, 127.30, 127.25, 127.12, 127.01, 125.10, 123.32, 118.11, 118.01, 115.91, 115.60, 115.00, 114.93, 114.72, 102.39, 84.93, 84.80, 82.56, 78.82, 78.55, 77.95, 75.99 (CH), 75.60, 75.31 (CH_2), 75.15 (CH), 74.96, 74.76 (CH_2), 74.23, 73.77 (CH), 73.21, 73.08, 68.97, 67.62 (CH_2), 61.02, 60.57, 60.39 (CH), 51.26, 38.02 (CH_2), 25.85 (CH_3), 24.67 (CH_2), 18.19 (C), -4.56, -4.87 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$) δ: -114.94 (1F, septet, *J* = 4.3 Hz), -117.10 (1F, septet, *J* = 4.3 Hz). MALDI-MS ($C_{92}H_{99}F_2NO_{15}SiS$): $[MNa]^+$ 1578.6365 (calcd. 1578.6370).



β-Lactam 14B. Sulfonate **14A** (166 mg 4:1 mixture) was dissolved in EtOH (5 mL), $Pd(OH)_2$/C (20% (w/w), 94 mg) was added and the suspension was evacuated 4 times with H_2 and stirred under an H_2-atmosphere for 11.5 h. The suspension was evaporated on celite and purified by dry column vacuum chromatography (4.3 x 2.0 cm) on silica gel eluting with a gradient of 0-10% MeOH in CH_2Cl_2 (v/v) to give β-lactam **14B** (69.5 mg, 52% from **11**) as a colourless oil.

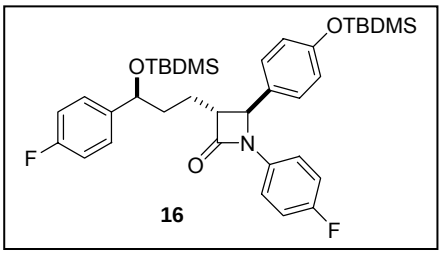
R_f (20% MeOH in CH_2Cl_2 (v/v)) 0.46; ^{1}H-NMR (300 MHz, CD_3OD) δ: 7.46-7.38 (4H, m), 7.31-7.23 (4H, m), 7.04-6.95 (4H, m), 4.75-4.68 (1H, m), 4.44 (1H, d, *J* = 8.1 Hz), 3.92-3.80 (5H, m), 3.69-3.18 (11H, m), 3.10-3.05 (1H, m), 1.95-1.75 (4H, m), 0.86 (9H, s), 0.01 (3H, s), -0.19 (3H, s). ^{13}C-NMR (75 MHz, CD_3OD) δ: 169.31, 169.21, 161.76, 158.91, 150.96, 142.28, 138.45, 135.01, 134.98, 131.06, 130.95 (C), 128.83, 124.50, 119.92, 119.83, 116.99, 116.68, 116.10, 116.04, 115.81, 115.74, 104.54, 80.33, 80.10, 78.11, 77.81, 77.72, 76.30, 75.13, 74.89, 73.61, 71.38 (CH), 62.47, 61.63 (CH_2), 61.56, 61.47 (CH), 53.26, 38.83 (CH_2), 26.38 (CH_3), 25.75 (CH_2), 19.04 (C), -4.40, -4.70 (CH_3). ^{19}F-NMR (282 MHz, CD_3OD) δ: -117.94 (1F, septet, *J* = 4.3 Hz), -120.10 (1F, septet, *J* = 4.3 Hz). MALDI-MS ($C_{43}H_{57}F_2NO_{15}SiS$): $[MNa]^+$ 948.3088 (calcd. 948.3084).



β-Lactam 14. β-Lactam **14B** (59.5 mg, 0.073 mmol) was dissolved in anhydrous THF (2.0 mL, teflon bottle), anhydrous pyridine (0.40 mL) followed by HF·pyridine complex (0.40 mL) were added and the solution was stirred for 14 h. Sat. aq. $NaHCO_3$ (5 mL) was added and the

suspension was evaporated on celite and purified by dry column vacuum chromatography (4.4 x 2.0 cm) on silica gel eluting with a gradient of 10-20% MeOH in CH_2Cl_2 (v/v) to give β-lactam **14** (38.1 mg, 64%) as a white solid.

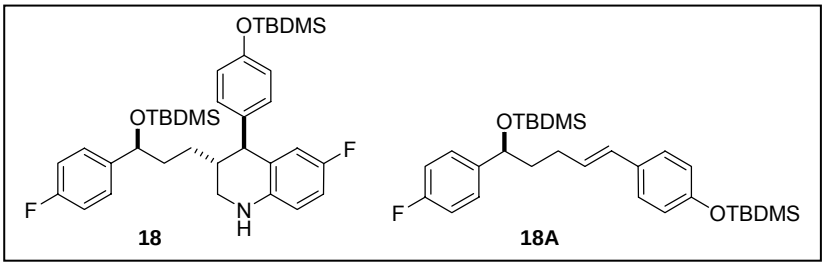
R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.17 (eluted thrice); ^{1}H-NMR (300 MHz, CD_3OD) δ: 7.45 (2H, t, *J* = 9.3 Hz), 7.40 (2H, d, *J* = 8.7 Hz), 7.33-7.24 (4H, m), 7.02 (2H, t, *J* = 8.1 Hz), 6.98 (2H, d, *J* = 8.7 Hz), 4.90 (1H, d, *J* = 1.9 Hz), 4.60 (1H, dd, *J* = 5.0, 6.2 Hz), 4.43 (1H, d, *J* = 7.5 Hz), 3.92-3.79 (5H, m), 3.69-3.49 (4H, m), 3.44-3.18 (6H, m), 3.12-3.06 (1H, m), 1.99-1.82 (4H, m). ^{13}C-NMR (75 MHz, CD_3OD) δ: 169.31, 165.08, 162.17, 161.85, 158.96, 150.98, 142.15, 138.51, 135.01 (C), 128.88, 128.76, 124.46, 119.97, 119.86, 116.99, 116.68, 116.13, 115.84, 104.54, 80.35, 80.06, 78.11, 77.81, 77.71, 76.31, 74.91, 73.77, 73.63, 71.39 (CH), 62.45, 61.50 (CH_2), 61.42 (CH), 53.26, 37.45, 26.12 (CH_2). ^{19}F-NMR (282 MHz, CD_3OD) δ: -118.08 (1F, septet, *J* = 4.3 Hz), -120.21 (1F, septet, *J* = 4.3 Hz). MALDI-MS ($C_{37}H_{43}F_2NO_{15}S$): $[MNa]^+$ 834.2223 (calcd. 834.2219).



16

Silyl ether 16. Ezetimibe **10**[11] (279 mg, 0.681 mmol) was dissolved in anhydrous DMF (5 mL), imidazole (262 mg, 3.84 mmol) and TBDMSCl (500 mg, 3.32 mmol) were added sequentially and the solution was stirred for 5 h followed by addition of 50% sat. aq. $NaHCO_3$ (50 mL). After extraction with EtOAc (4 x 20 mL), the combined organic layer was washed successively with sat. aq. $NaHCO_3$ (20 mL) and H_2O (20 mL), evaporated on celite and purified by dry column vacuum chromatography (3.8 x 3.3 cm) on silica gel eluting with a gradient of 0-10% EtOAc in hexane (v/v) to give silyl ether **16** (424 mg, 97%) as a colourless oil.

R_f (1:3 EtOAc/hexane (v/v)) 0.65; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.25-7.21 (4H, m), 7.17 (2H, d, *J* = 8.1 Hz), 6.98 (2H, t, *J* = 8.7 Hz), 6.91 (2H, t, *J* = 8.7 Hz), 6.83 (2H, d, *J* = 8.1 Hz), 4.66 (1H, t, *J* = 5.6 Hz), 4.51 (1H, d, *J* = 2.5 Hz), 3.08-3.02 (1H, m), 1.96-1.78 (4H, m), 0.98 (9H, s), 0.88 (9H, s), 0.20 (6H, s), 0.02 (3H, s), -0.16 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 167.27, 163.28, 160.27, 160.04, 157.06, 155.71, 140.58, 140.54, 133.89, 133.86 (C), 129.99, 127.22, 127.11, 126.94, 120.56, 118.24, 118.15, 115.74, 115.44, 114.99, 114.72 (CH), 73.84, 61.08, 60.44 (CH), 38.08 (CH_2), 25.90, 25.68 (CH_3), 24.75 (CH_2), 18.26, 18.24 (C), -4.28, -4.52, -4.83 (CH_3). IR (cm^{-1}): 2954, 2930, 2858, 1752, 1607, 1510, 1385, 1259, 1223, 1101, 1085, 914, 834, 778. MALDI-MS ($C_{36}H_{49}F_2NO_3Si_2$): $[MH\text{-}TBDMSOH]^+$ 506.2329 (calcd. 506.2327); $[MH]^+$ 638.3289 (calcd. 638.3297); $[MNa]^+$ 660.3117 (calcd. 660.3117). Anal. Calcd for $C_{36}H_{49}F_2NO_3Si_2$: C, 67.78; H, 7.74; N, 2.20. Found: C, 67.70; H, 7.60; N, 2.02.



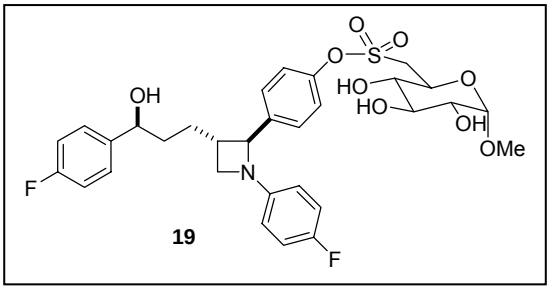
18 **18A**

Bicycle 18. $LiAlH_4$ (57 mg, 1.5 mmol) and $AlCl_3$ (200 mg, 1.5 mmol) were suspended in anhydrous ether (15 mL), refluxed for 40 min and cooled to 0°C. Azetidinone **32** (180.8 mg, 0.283 mmol) dissolved in anhydrous ether (5 mL) was added and after stirring at 0°C for 30 min, H_2O (1 mL) was added dropwise. The suspension was evaporated on celite and purified by dry column vacuum chromatography (3.5 x

3.3 cm) on silica gel eluting with a gradient of 0-50% CH_2Cl_2 in hexane (v/v) to give bicycle **18** (110.8 mg, 63%) and olefin **18A** (24.1 mg, 16%) as colourless oils.

18: R_f (1:9 EtOAc/hexane (v/v)) 0.23; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.18-7.14 (2H, m), 6.95 (2H, t, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.7 Hz), 6.74 (2H, d, *J* = 8.1 Hz), 6.68 (1H, dd, *J* = 2.8, 8.4 Hz), 6.44 (1H, dd, *J* = 6.5, 8.7 Hz), 6.38 (1H, dd, *J* = 2.8, 9.6 Hz), 4.48 (1H, dd, *J* = 5.0, 6.8 Hz), 3.78 (1H, bs), 3.61 (1H, d, *J* = 7.5 Hz), 3.26 (1H, dd, *J* = 3.1, 11.2 Hz), 2.91 (1H, dd, *J* = 7.8, 11.5 Hz), 1.91-1.85 (1H, m), 1.68-1.44 (3H, m), 1.16-1.04 (1H, m), 0.99 (9H, s), 0.80 (9H, s), 0.20 (6H, s), 0.06 (3H, s), -0.21 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 163.60, 160.36, 157.37, 154.27, 141.53, 141.01, 138.13 (C), 130.07, 127.56, 127.46, 125.58, 125.50, 120.01, 117.27, 116.98, 115.17, 114.89, 114.78, 114.08, 113.79 (CH), 74.64, 48.97 (CH), 44.52 (CH_2), 39.89 (CH), 38.67, 28.28 (CH_2), 26.00, 25.90 (CH_3), 18.38, 18.32 (C), -4.16, -4.43, -4.77 (CH_3). IR (cm^{-1}): 2955, 2930, 2858, 1607, 1506, 1472, 1408, 1361, 1258, 1222, 1170, 1144, 1085, 1006, 915, 837, 808, 779, 735, 667. MALDI-MS ($C_{36}H_{51}F_2NO_2Si_2$): $[MH\text{-}TBDMSOH]^+$ 492.2517 (calcd. 492.2534); $[M]^+$ 623.3414 (calcd. 623.3426). Anal. Calcd for $C_{36}H_{51}F_2NO_2Si_2$: C, 69.30; H, 8.24; N, 2.24. Found: C, 69.47; H, 8.32; N, 2.15.

18B: R_f (1:9 EtOAc/hexane (v/v)) 0.70; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.29-7.25 (2H, m), 7.18 (2H, t, *J* = 8.7 Hz), 6.19 (2H, t, *J* = 8.7 Hz), 6.76 (2H, d, *J* = 8.7 Hz), 6.30 (1H, d, *J* = 15.6 Hz), 6.04 (1H, dd, *J* = 6.8, 15.6 Hz), 4.68 (1H, dd, *J* = 5.0, 7.5 Hz), 2.26-2.13 (2H, m), 1.91-1.66 (2H, m), 0.98 (9H, s), 0.89 (9H, s), 0.19 (6H, s), 0.04 (3H, s), -0.16 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 163.42, 160.18, 154.72, 141.28, 131.10, 129.49 (C), 128.25, 127.42, 127.32, 126.87, 120.10, 114.97, 114.69, 73.85 (CH), 40.64, 28.94 (CH_2), 25.84, 25.68 (CH_3), 18.22, 18.18 (C), -4.42, -4.60, -4.91 (CH_3). IR (cm^{-1}): 3030, 2956, 2930, 2887, 2858, 1605, 1509, 1472, 1362, 1258, 1223, 1169, 1155, 1088, 1006, 965, 915, 837, 804, 779, 701, 665.

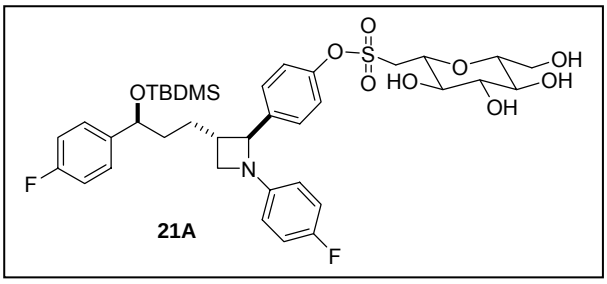


19

Azetidine 19. $LiAlH_4$ (57 mg, 1.5 mmol) and $AlCl_3$ (200 mg, 1.5 mmol) were suspended in anhydrous ether (15 mL), refluxed for 30 min and cooled to 0°C. β-Lactam **12** (26.8 mg, 0.041 mmol) dissolved in anhydrous THF (1 mL, 2 x 0.5 mL rinse) was added and after stirring at 0°C for 10 min, sat. aq. $NaHCO_3$ (1 mL) was added dropwise. The suspension was evaporated on celite and purified by dry column vacuum chromatography (4.7 x 2.0 cm) on silica gel eluting with a gradient of 0-12% MeOH in CH_2Cl_2 (v/v) to give azetidine **19** (20.4 mg, 78%) as a colourless oil.

R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.20; ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.63-7.59 (2H, m), 7.49-7.42 (2H, m), 7.36-7.29 (2H, m), 7.10-7.01 (2H, m), 6.92-6.77 (2H, m), 6.40-6.35 (2H, m), 4.72 (1H, d, *J* = 3.7 Hz), 4.62 (1H, d, *J* = 5.0 Hz), 4.61 (1H, bs), 4.52 (1H, d, *J* = 6.9 Hz), 4.31 (2H, t, *J* = 4.4 Hz), 4.21-4.15 (2H, m), 3.90 (1H, dd, *J* = 1.2, 14.9 Hz), 3.76 (1H, d, *J* = 8.1 Hz), 3.68 (1H, dd, *J* = 3.7, 9.3 Hz), 3.66-3.57 (2H, m), 3.41 (3H, s, OMe), 3.38-3.31 (1H, m), 3.25 (1H, dt, *J* = 5.0, 13.7 Hz), 2.62 (1H, dd, *J* = 6.8, 14.3 Hz), 1.92-1.84 (1H, m), 1.74-1.57 (3H, m). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 163.90, 160.69, 158.31, 155.22, 149.93, 149.72, 149.52, 142.90, 142.84 (C), 129.60, 129.44, 128.30, 128.24, 128.13, 123.51, 122.99, 115.95, 115.91, 115.66, 115.40, 115.11, 113.87, 113.77, 113.67, 113.57 (CH), 100.84, 74.86, 74.03, 73.68, 73.14, 72.87, 68.09 (CH), 56.67 (CH_2), 55.63 (CH_3), 52.83 (CH_2), 42.78 (CH), 37.60, 29.83 (CH_2). IR (cm^{-1}): 3390, 2935, 2850, 1605, 1508, 1474, 1366, 1221, 1147, 1052, 1015, 874, 824, 755. MALDI-MS ($C_{31}H_{35}F_2NO_9S$):

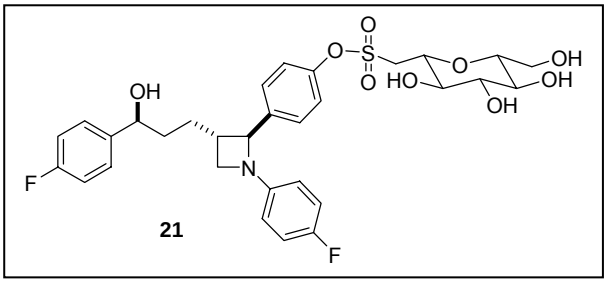
$[MH\text{-}H_2O]^+$ 618.1968 (calcd. 618.1973); $[MH]^+$ 636.2045 (calcd. 636.2079); $[MNa]^+$ 658.1901 (calcd. 658.1898).



21A

Azetidine 21A. $LiAlH_4$ (57 mg, 1.5 mmol) and $AlCl_3$ (200 mg, 1.5 mmol) were suspended in anhydrous ether (15 mL), refluxed for 30 min and cooled to 0°C. β-Lactam **20** (41.3 mg, 0.054 mmol) dissolved in anhydrous ether (5 mL) was added and after stirring at 0°C for 10 min, sat. aq. $NaHCO_3$ (1 mL) was added dropwise. The suspension was evaporated on celite and purified by dry column vacuum chromatography (4.2 x 2.0 cm) on silica gel eluting with a gradient of 0-20% MeOH in CH_2Cl_2 (v/v) to give azetidine **21A** (38.2 mg, 94%) as a white foam.

R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.31; ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.58 (2H, d, *J* = 8.7 Hz), 7.47 (2H, d, *J* = 8.7 Hz), 7.29 (2H, dd, *J* = 5.6, 8.7 Hz), 7.05 (2H, t, *J* = 8.7 Hz), 6.88 (2H, t, *J* = 9.0 Hz), 6.37 (2H, dd, *J* 4.7, 9.0 Hz), 4.71 (1H, t, *J* = 5.5 Hz), 4.61 (1H, d, *J* = 5.0 Hz), 4.49 (2H, d, *J* = 6.8 Hz), 4.30 (1H, bs), 4.17 (1H, t, *J* = 7.2 Hz), 3.92-3.83 (3H, m), 3.74-3.66 (1H, m), 3.57-3.40 (5H, m), 3.32-3.15 (2H, m), 2.63-2.56 (1H, m), 1.82-1.56 (4H, m), 0.87 (9H, s), 0.04 (3H, s), -0.17 (3H, s). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 164.97, 161.76, 159.31, 156.21, 150.76, 150.47, 150.45, 143.77, 143.11, 143.07 (C), 129.35, 129.22, 124.60, 116.95, 116.65, 116.48, 116.19, 114.86, 114.75 (CH), 82.15, 80.21, 76.81, 75.43, 74.99, 74.52, 72.41 (CH), 63.70, 57.54, 53.95 (CH_2), 43.62 (CH), 39.47, 31.22 (CH_2), 27.20 (CH_3), 19.70 (C), -3.40, -3.68 (CH_3). IR (cm^{-1}): 3377, 2930, 2856, 1605, 1508, 1472, 1361, 1252, 1222, 1147, 1090, 1015, 871, 836, 776, 760. MALDI-MS ($C_{37}H_{49}F_2NO_9SSi$): $[MNa]^+$ 772.2767 (calcd. 772.2763).



21

Azetidine 21. Azetidine **21A** (34.3 mg, 0.046 mmol) was dissolved in anhydrous THF (2.5 mL, teflon bottle), anhydrous pyridine (0.5 mL) followed by HF·pyridine complex (0.5 mL) were added and the solution was stirred for 14 h, diluted with ether (20 mL) and washed with sat. aq. $NaHCO_3$ (3 x 5 mL). The organic layer was evaporated on celite and purified by dry column vacuum chromatography (4.9 x 2.0 cm) on silica gel eluting with a gradient of 0-18% MeOH in CH_2Cl_2 (v/v) to give azetidine **21** (20.2 mg, 69%) as a colourless oil.

R_f (10% MeOH in CH_2Cl_2 (v/v)) 0.24; ^{1}H-NMR (300 MHz, acetone-d_6) δ: 7.61 (2H, d, *J* = 8.1 Hz), 7.48 (2H, d, *J* = 8.7 Hz), 7.30 (2H, dd, *J* = 5.6, 8.7 Hz), 7.04 (2H, t, *J* = 8.7 Hz), 6.89 (2H, m), 6.38 (2H, dd, *J* = 4.4, 8.7 Hz), 4.60 (2H, d, *J* = 4.4 Hz), 4.52 (1H, d, *J* = 6.8 Hz), 4.45 (1H, d, *J* = 2.5 Hz), 4.29 (2H, d, *J* = 4.4 Hz), 4.19 (1H, t, *J* = 6.8 Hz), 4.03-3.83 (3H, m), 3.80-3.67 (1H, m), 3.60-3.31 (6H, m), 3.25 (1H, p, *J* = 4.4 Hz), 2.62 (1H, dd, *J* = 7.5, 14.3 Hz), 1.92-1.82 (1H, m), 1.78-1.61 (3H, m). ^{13}C-NMR (75 MHz, acetone-d_6) δ: 164.04, 155.14, 149.92, 149.71, 149.47, 142.77, 129.48 (C), 128.19, 128.16, 128.05, 123.52, 123.03, 115.87, 115.58, 115.39, 115.32, 115.05, 113.78, 113.69, 113.61, 113.51 (CH), 81.09, 79.15, 75.76, 73.98, 73.46, 72.75, 71.36 (CH), 62.63, 56.60, 52.88 (CH_2), 42.68 (CH), 37.52, 29.61 (CH_2). IR (cm^{-1}): 3370, 2933, 1605, 1508, 1474, 1360, 1220, 1146, 1087, 1015, 873, 823, 771. MALDI-MS ($C_{31}H_{35}F_2NO_9S$): $[MH\text{-}H_2O]^+$ 618.1973 (calcd. 618.1973); $[M]^+$ 635.1996 (calcd. 635.2001); $[MNa]^+$ 658.1900 (calcd. 658.1898).

The brush border membrane vesicle assay.[10]

Materials. Egg phosphatidylcholine was purchased from Avanti Polar Lipids (US), cholesterol oleate and cholesterol from Sigma, phosphate-buffered saline (PBS) from Invitrogen Corporation, [1α,2α(N)-^{3}H]cholesterol oleyl ether (37 Ci/mmol), [4-^{14}C-cholesterol] and Sepharose CL-4B from Amersham Biosciences, the BCA protein assay kit from Pierce (US) and the glucose dehydrogenase kit from Diagnostic Systems (Germany).

Preparation of Brush Border Membrane Vesicles. Brush border membrane vesicles were prepared and characterized [total protein content by the BCA method, sucrase activity and lipid uptake (4.2 mg protein/mL, 0.20 mg SUV/mL – see below)] essentially as previously described.[12] The source was small intestine (stored at -78 °C) from freshly killed farm rabbits. The isolation buffer was 2 mM Tris-HCl plus HCl to pH 7.1, 50 mM D-mannitol and 0.83 mM EGTA; 10 mM $MgC1_2$ was used in the precipitation step. The brush border pellet was redispersed in 12 mM Tris-HCl plus HCl to pH 7.1, 0.30 M D-mannitol and 5 mM EGTA.

Preparation of Small Unilamellar Vesicles (SUV). A total of 2 mg egg phosphatidylcholine and cholesteryl oleate (99:1 molar ratio) for control measurements and egg phosphatidylcholine, cholesteryl oleate and inhibitor (90:1:9 molar ratio) for inhibition experiments plus in either case a trace amount ^{3}H-labelled cholesteryl oleyl ether (or ^{14}C-labelled cholesterol) were dried from a chloroform-methanol solution (2:l v/v) by rotary evaporation. The lipid film was dried under high vacuum for at least 1 h and then dispersed in PBS buffer (2 mL). The suspension was sonicated with a microtip sonicator (Branson 250) for 1-1.5 h (output 2.2, 60% duty cycle).[13] After sonication, the vesicles were centrifuged (pressure 3.0, 3 min) in a Beckman airfuge and characterized by gel filtration (Sepharose CL-4B, 45 x 1 cm) as previously reported.[14]

Inhibition of Cholesterol Absorption by Brush Border Membrane Vesicles. Brush border membrane vesicles (5.0 mg protein/mL) were incubated at room temperature for 20 min with either control SUV (99:1 molar ratio egg phosphatidylcholine and cholesteryl oleate) or SUV containing inhibitors (90:1:9 molar ratio egg phosphatidylcholine, cholesteryl oleate and inhibitor). The experiment was terminated by centrifugation (pressure 3.0, 3 min) in a Beckman airfuge. The donor SUV remained in the supernatant under these conditions and the brush border membrane vesicles precipitated. The radioactivity present in both donor SUV and brush border membrane vesicles was counted in triplicate in a Beckman LS 7500 liquid scintillation counter.

% Inhibition was calculated from relative radioactivities in the supernatants and pellets according to the formula: Inhibition% = [(%Supernatant inhibitor SUV - %Supernatant control SUV) · 100%]/ %Pellet control SUV

The obtained inhibitions were: **10**:16±4% inhibition, **12**: 20±5% inhibition, **13**: 15±3% inhibition, **14**: 41±4% inhibition, **19**: 27±4% inhibition, **21**: 20±5% inhibition,.

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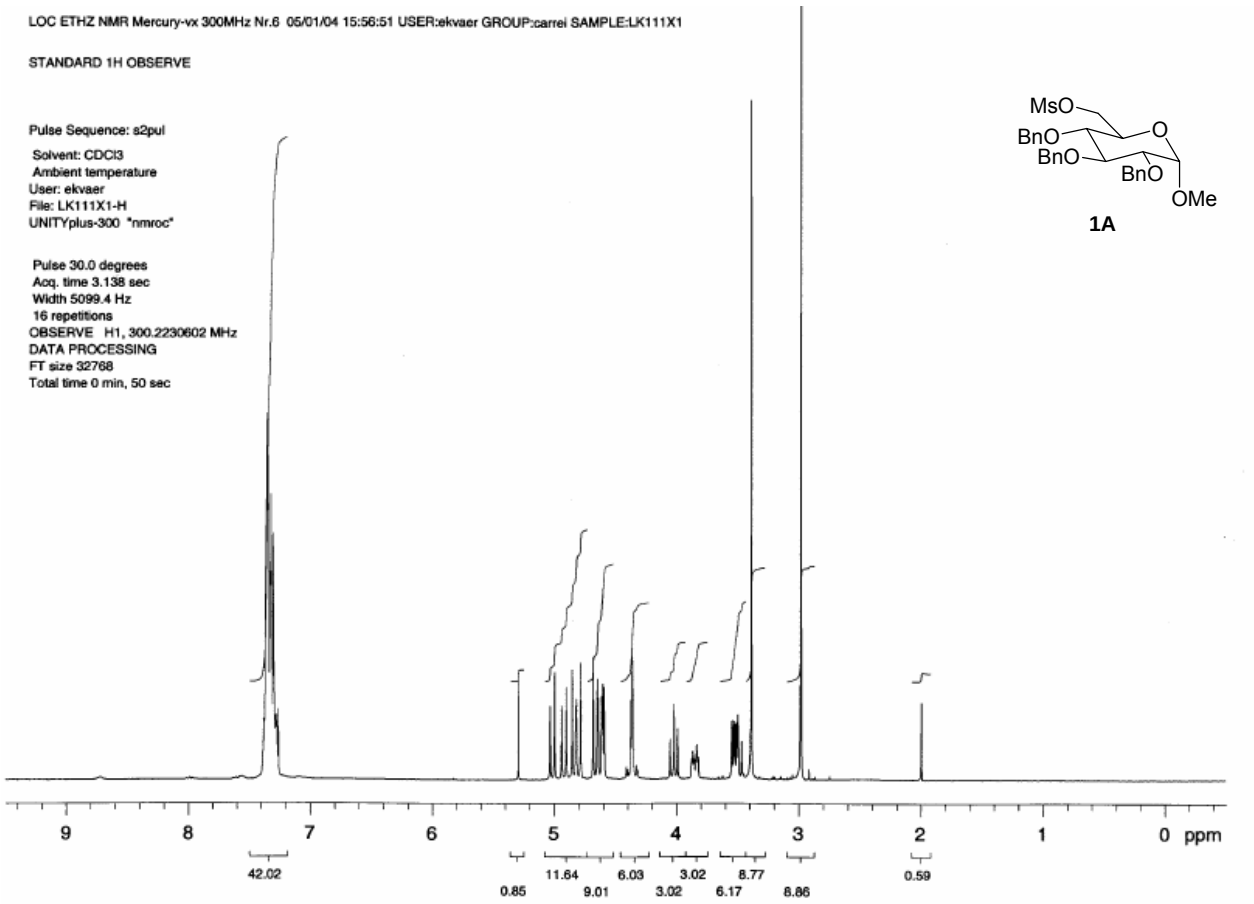
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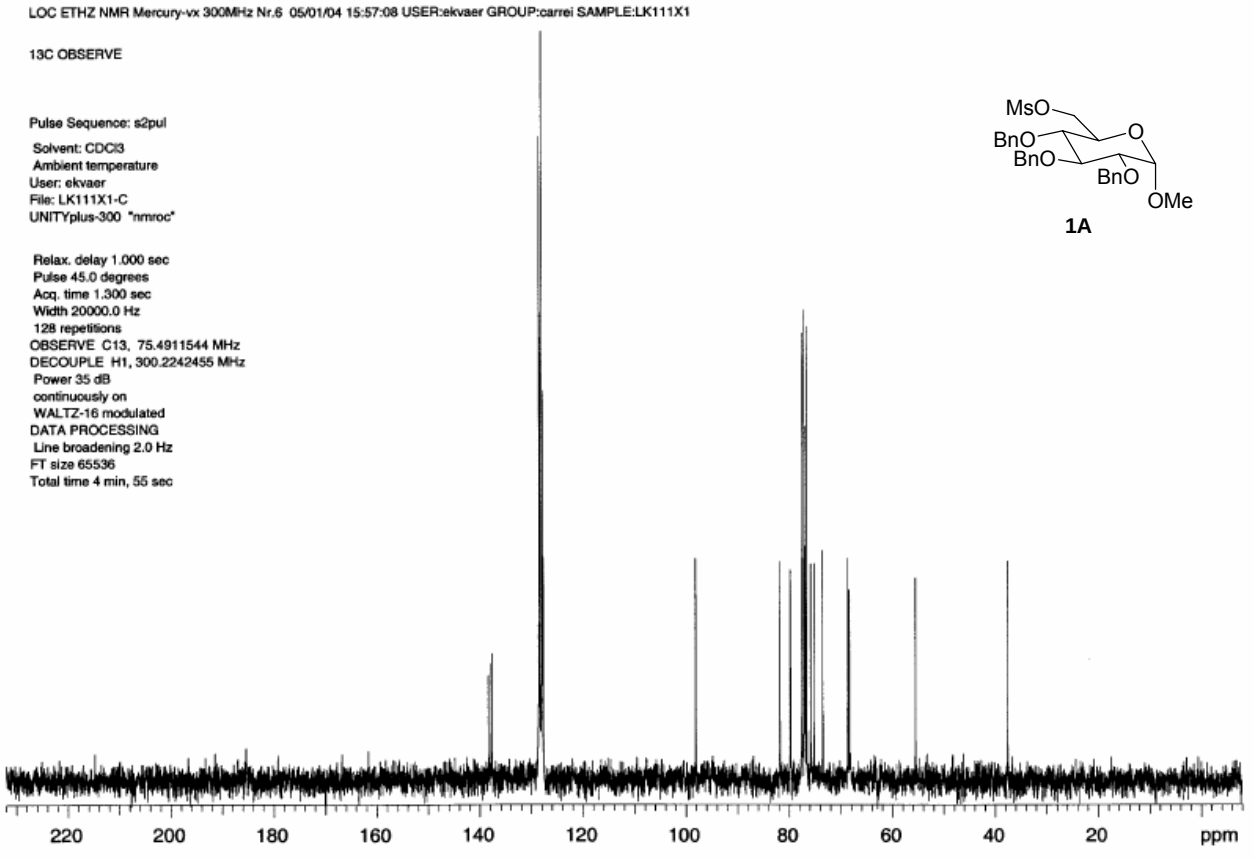
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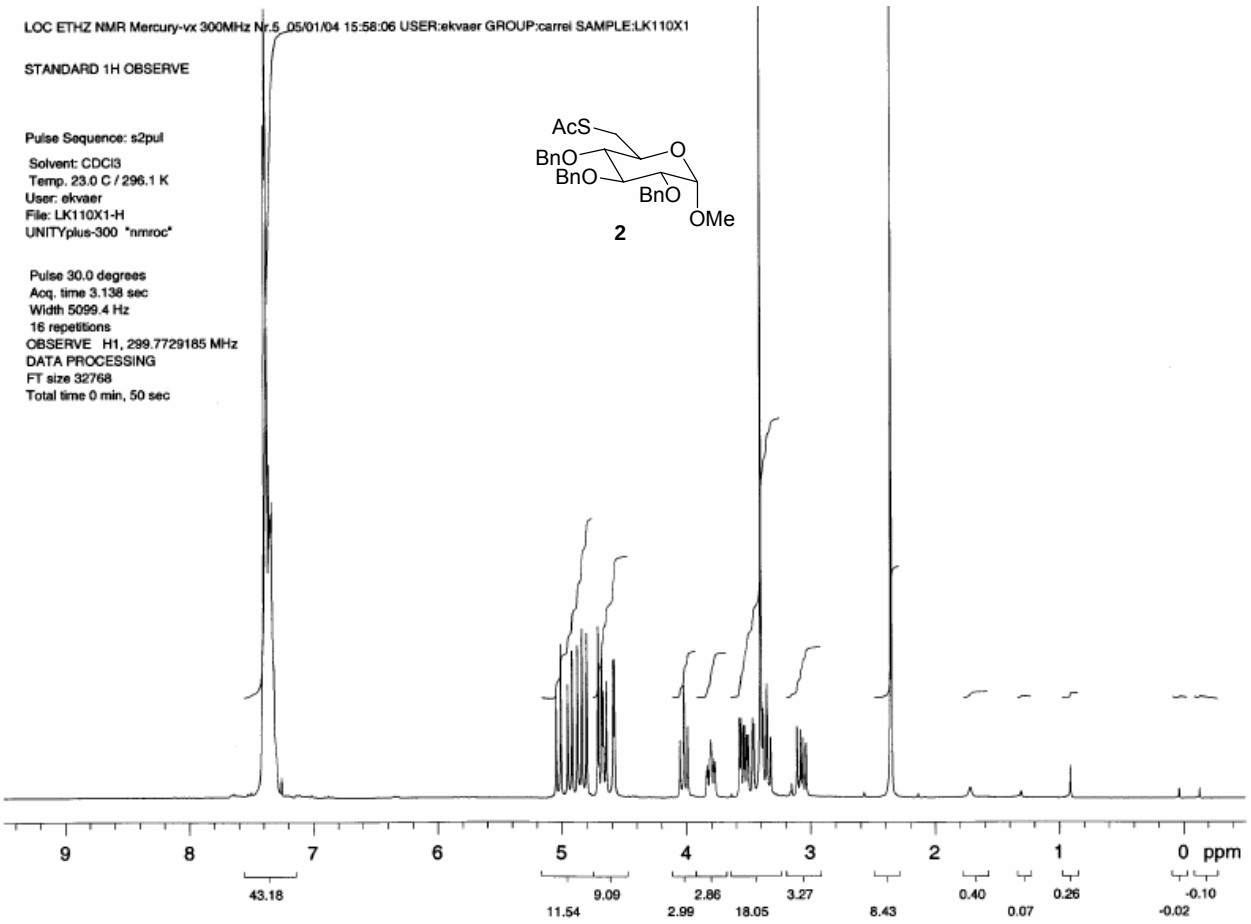
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BnO
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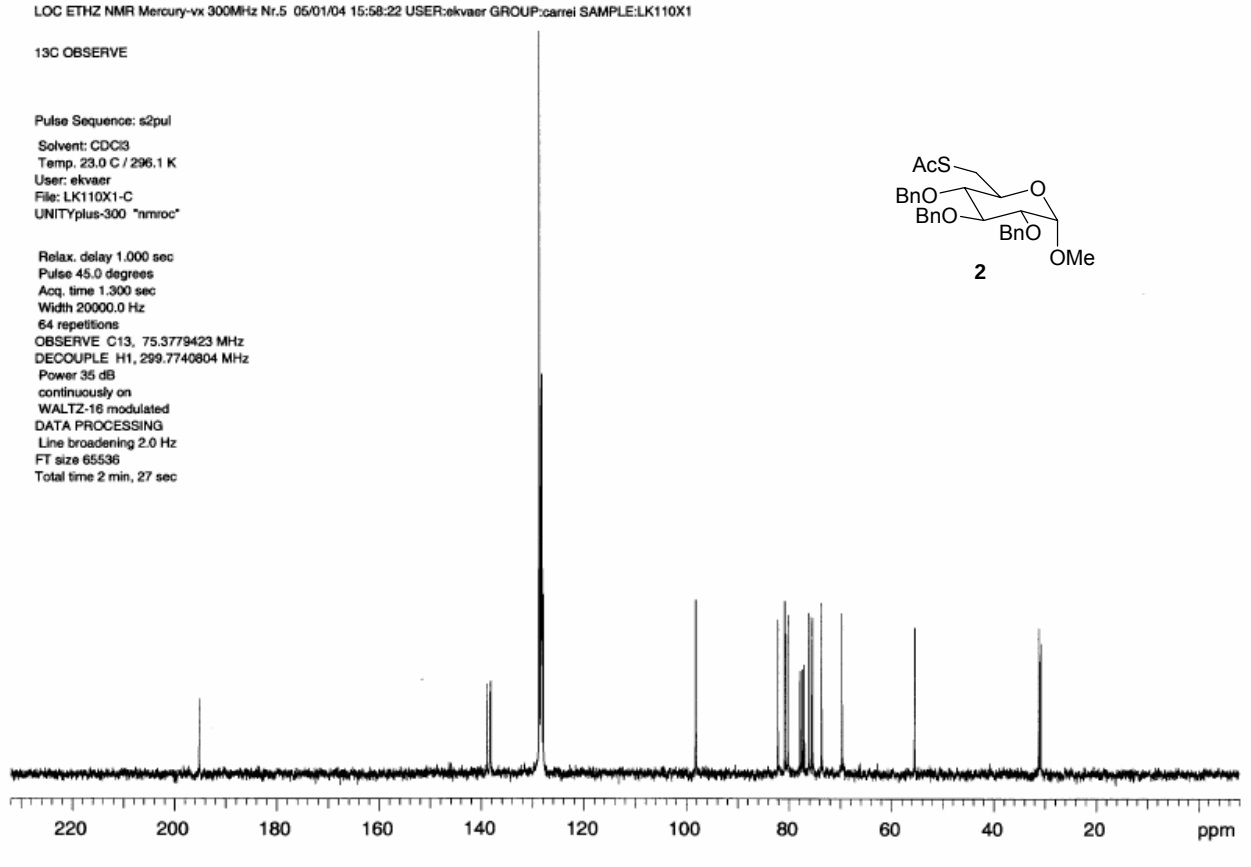
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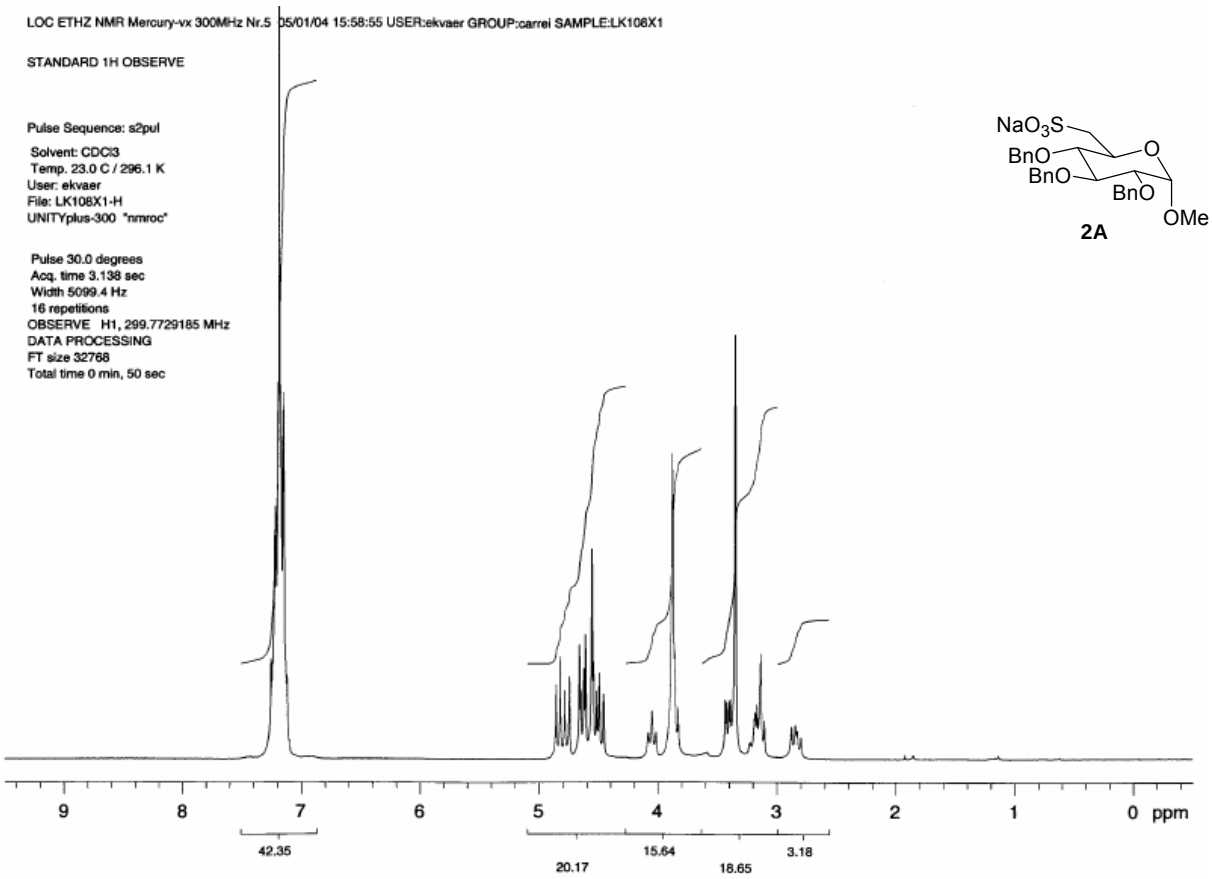
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2A
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4
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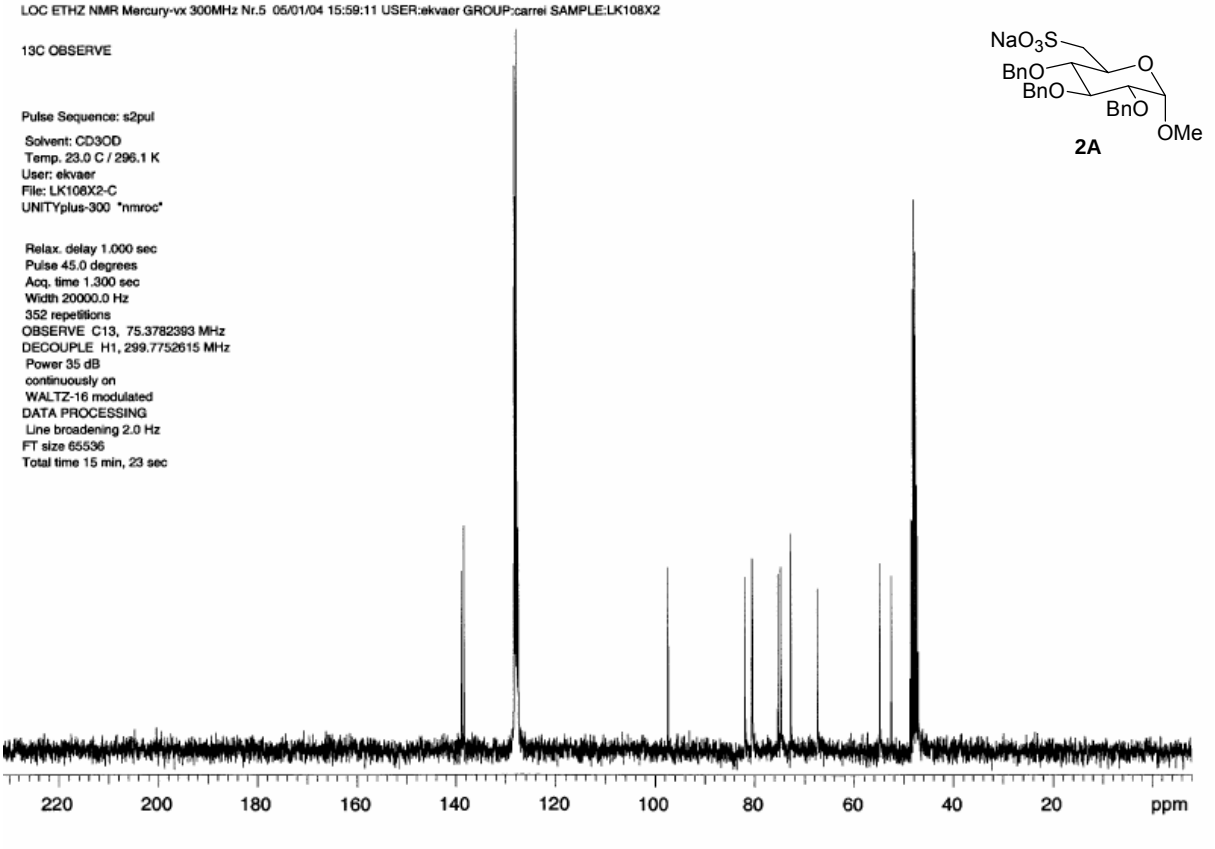
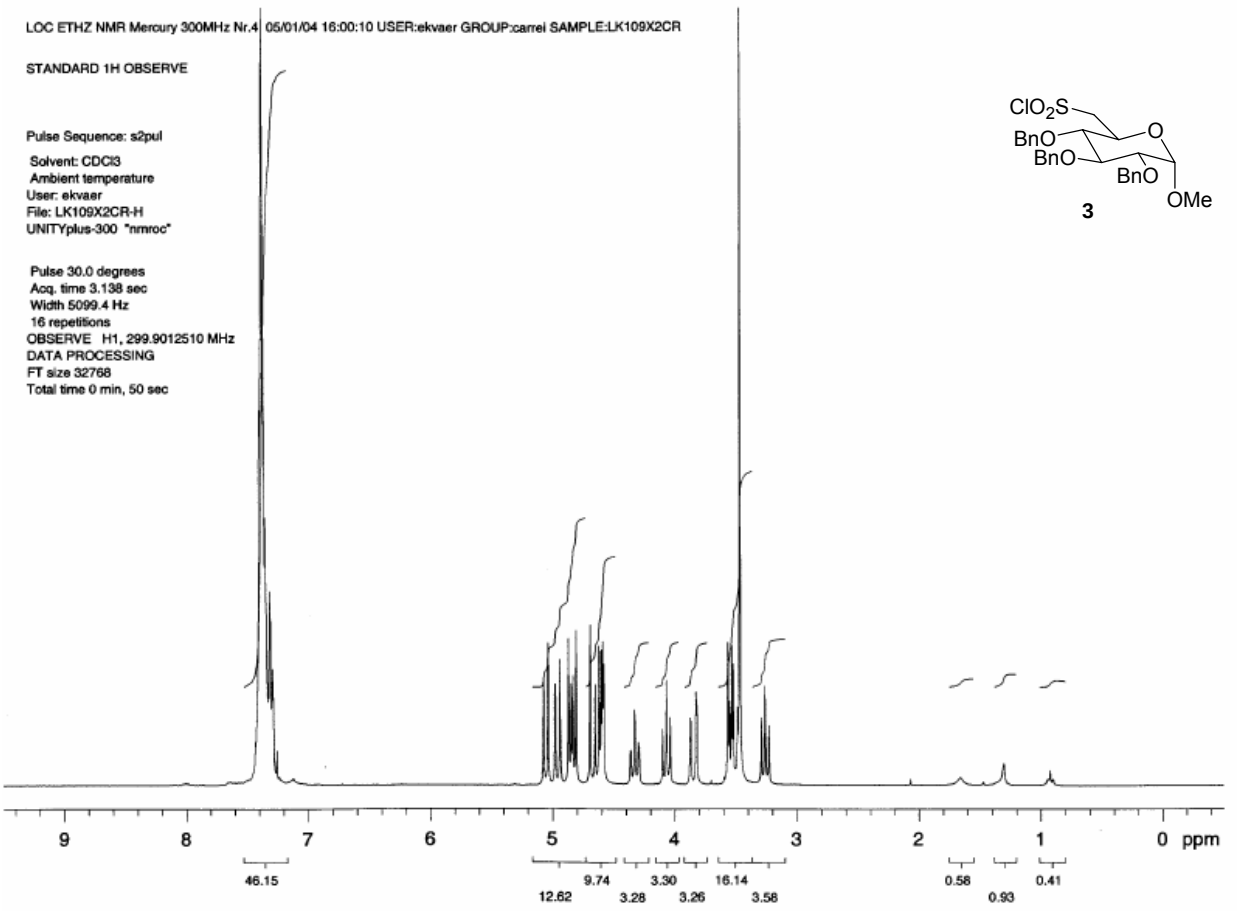
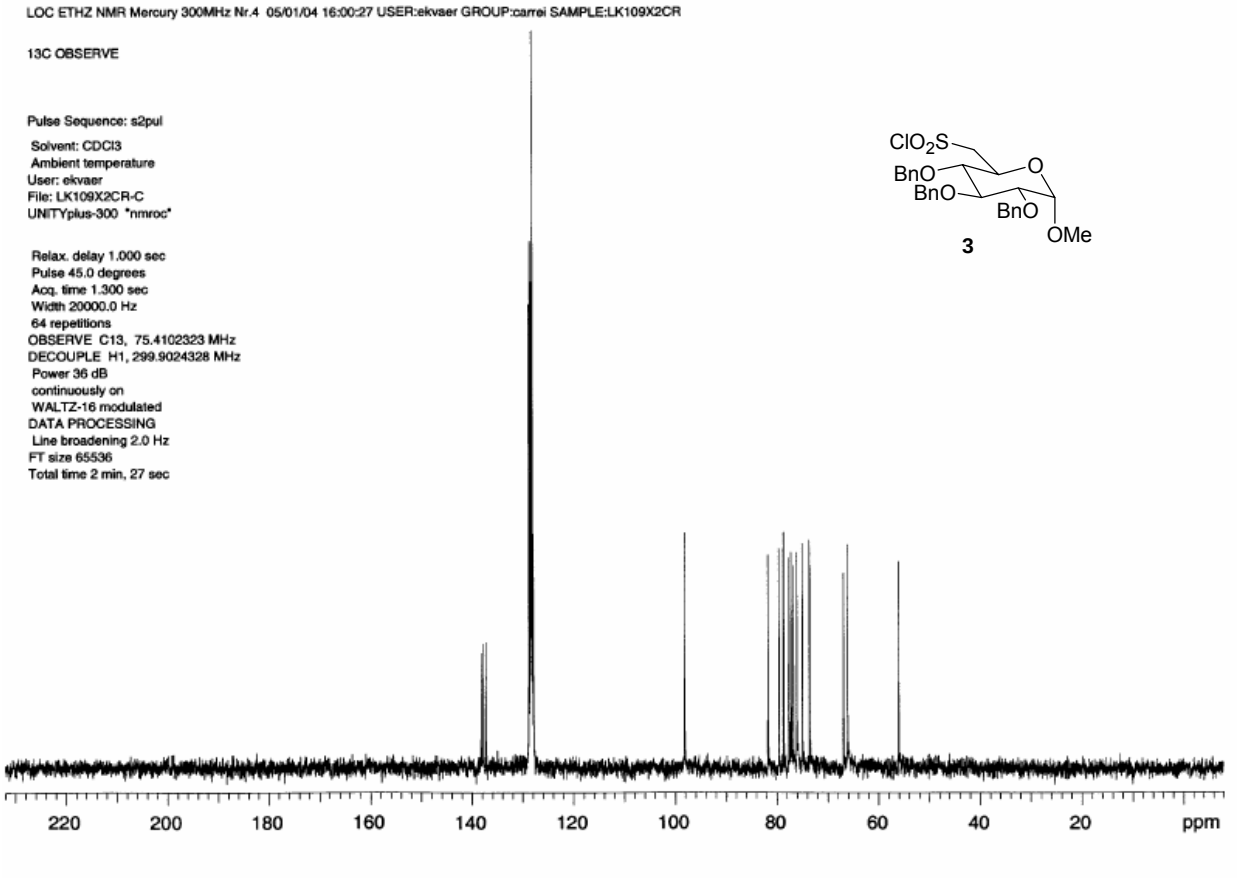
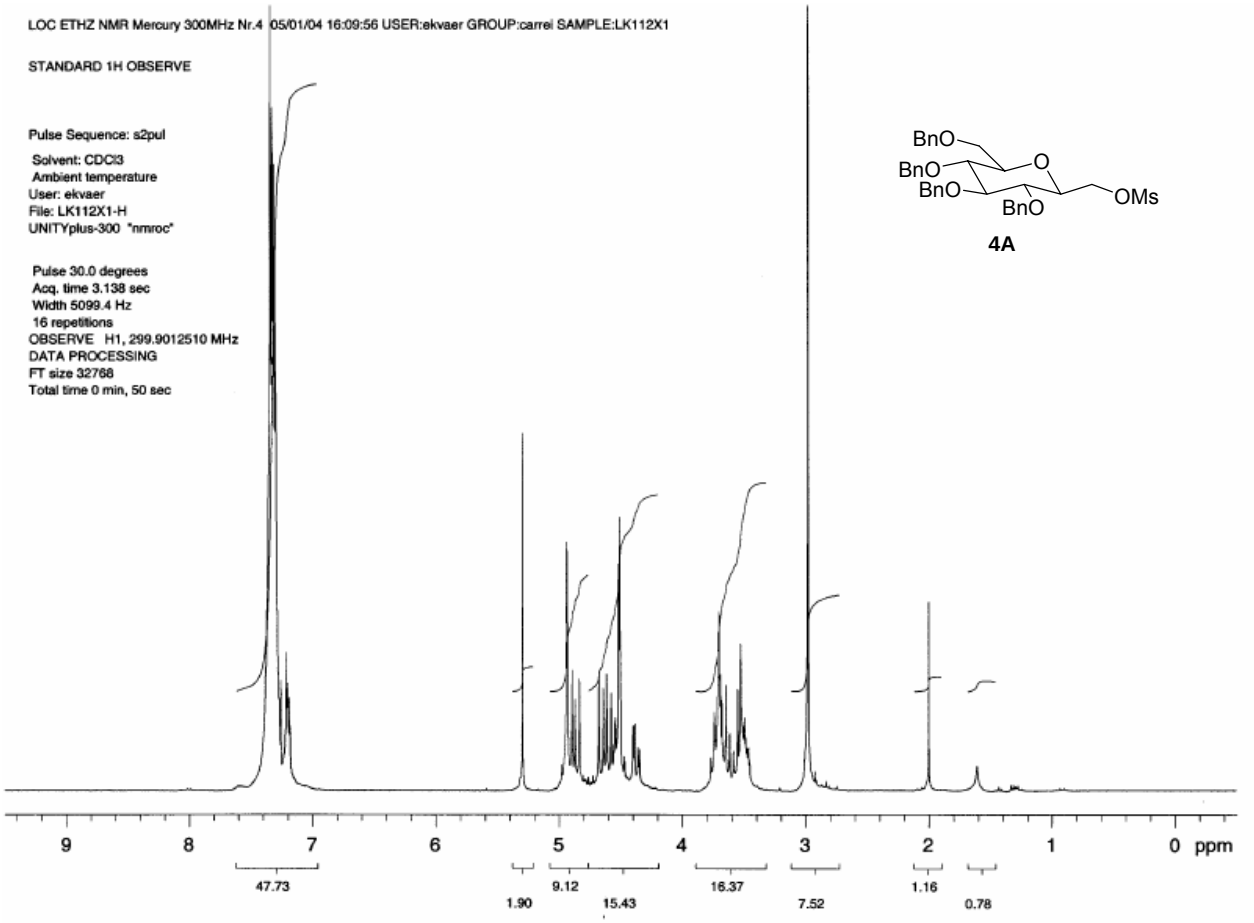
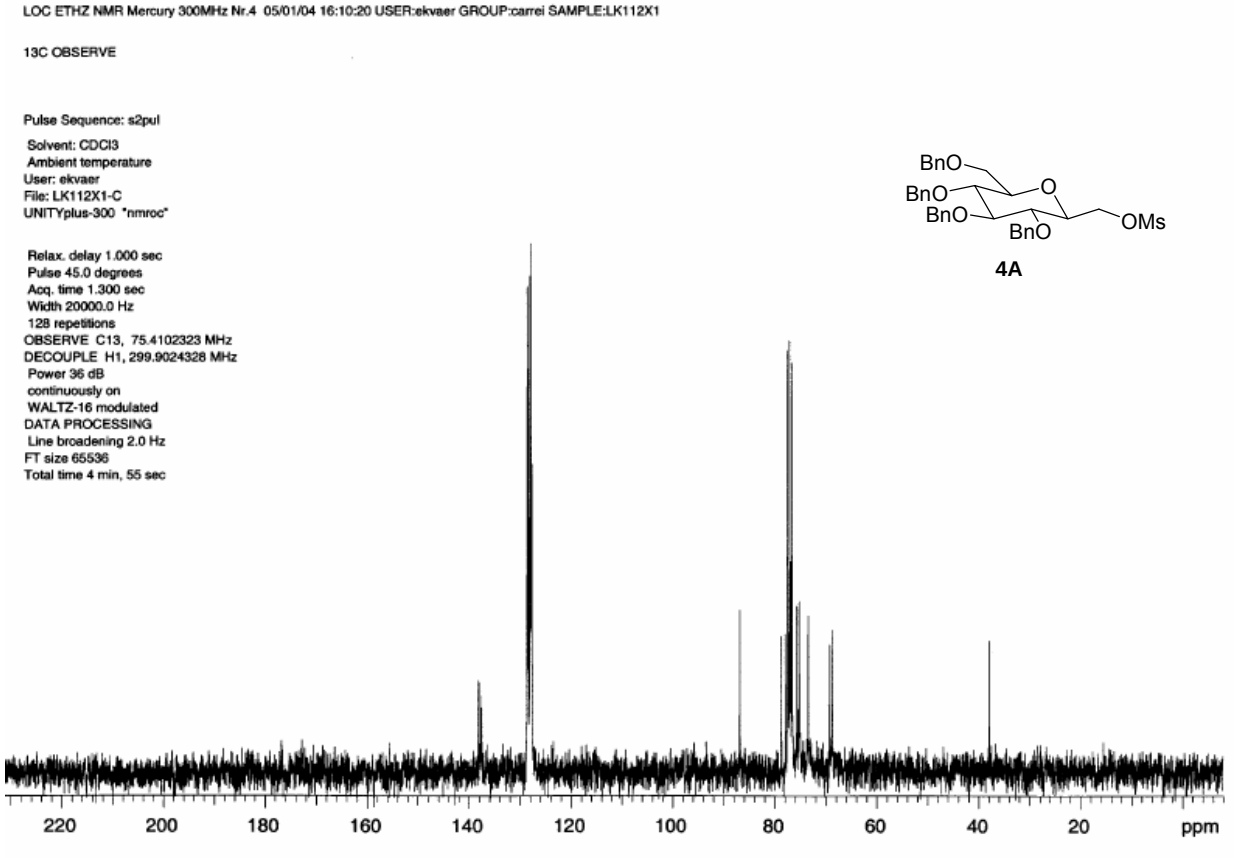
20.17
15.64
18.65
3.18

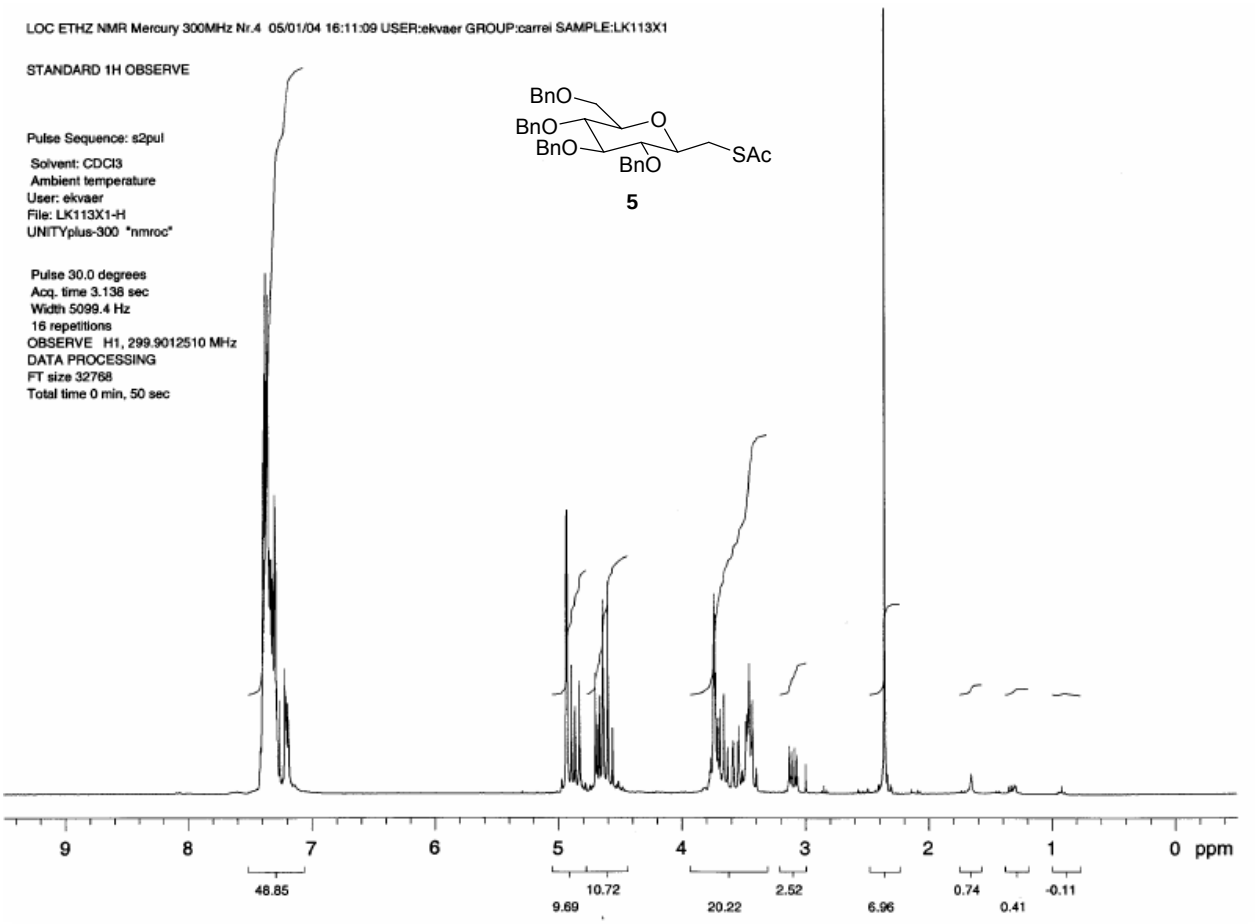

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 15:59:11 USER:ekvaer GROUP:carrei SAMPLE:LK108X2
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CD3OD
Temp. 23.0 C / 296.1 K
User: ekvaer
File: LK108X2-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
352 repetitions
OBSERVE C13, 75.3782393 MHz
DECOUPLE H1, 299.7752615 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 15 min, 23 sec
NaO3S
BnO
BnO
BnO
O
OMe
2A
220
200
180
160
140
120
100
80
60
40
20
ppm

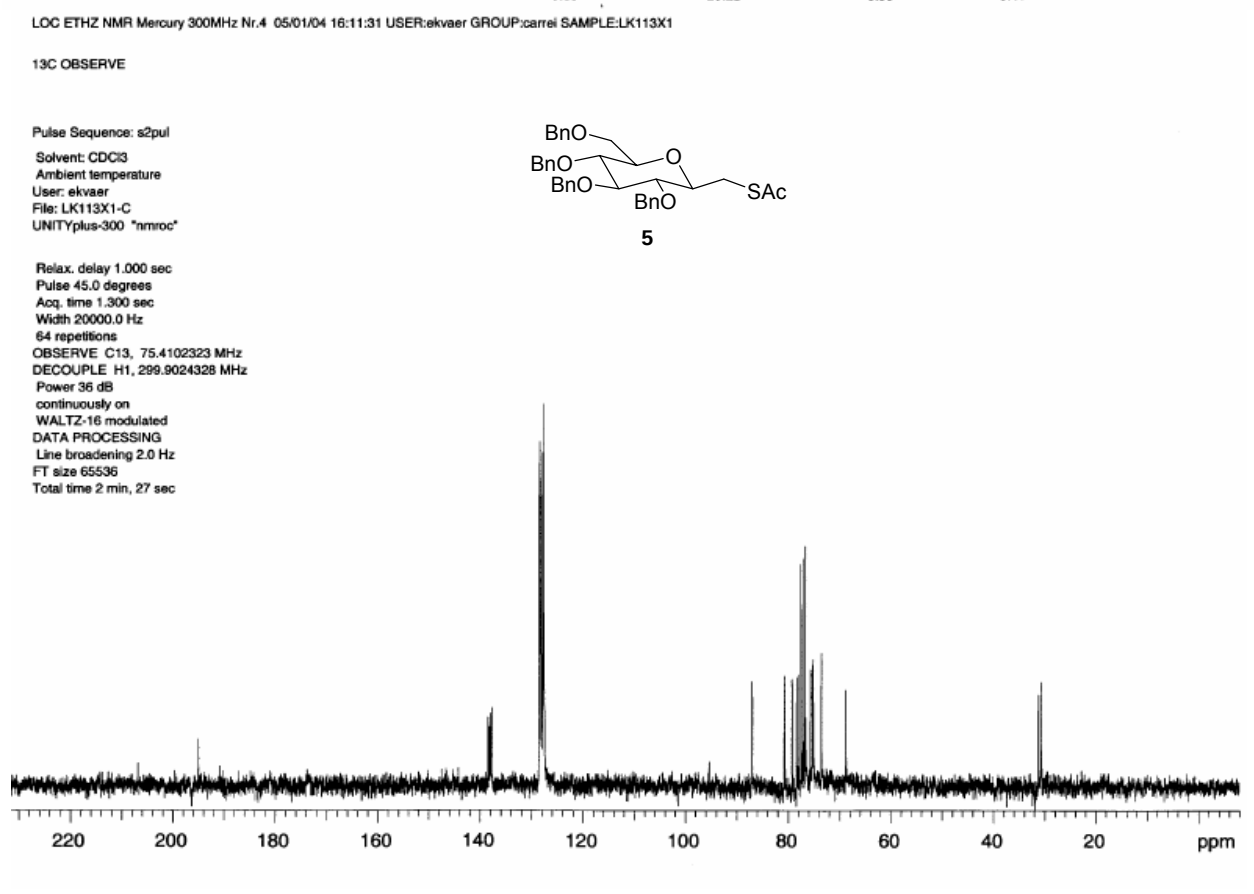

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:00:10 USER:ekvaer GROUP:carrei SAMPLE:LK109X2CR
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK109X2CR-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
ClO2S
BnO
BnO
BnO
O
OMe
3
9
8
7
6
5
4
3
2
1
0 ppm
46.15
12.62
9.74
3.28
3.30
3.26
16.14
3.58
0.58
0.93
0.41

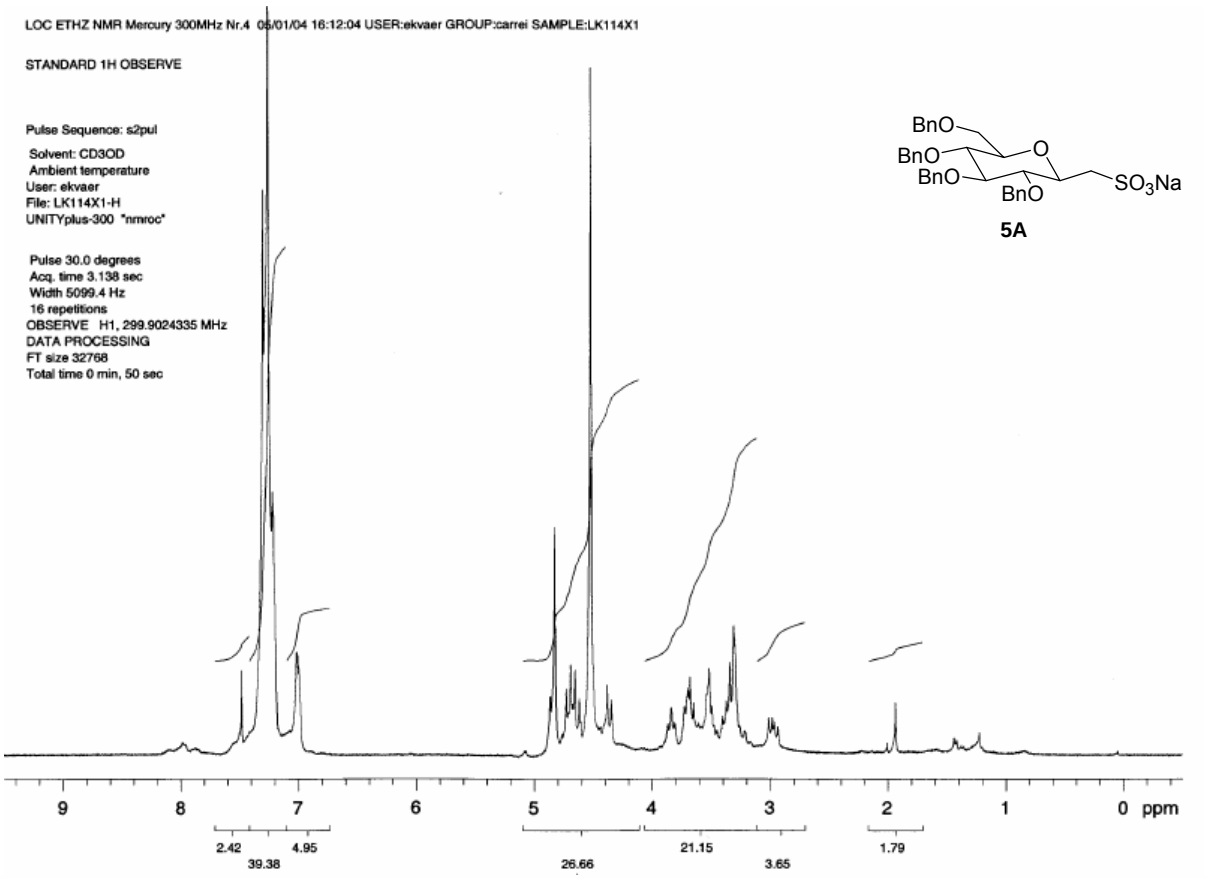

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:00:27 USER:ekvaer GROUP:carrei SAMPLE:LK109X2CR
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK109X2CR-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
64 repetitions
OBSERVE C13, 75.4102323 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 2 min, 27 sec
ClO2S
BnO
BnO
BnO
O
OMe
3
220
200
180
160
140
120
100
80
60
40
20
ppm


LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:09:56 USER:ekvaer GROUP:carrei SAMPLE:LK112X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK112X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
BnO
BnO
O
BnO
OMs
4A
9
8
7
6
5
4
3
2
1
0 ppm
47.73
1.90
9.12
15.43
16.37
7.52
1.16
0.78

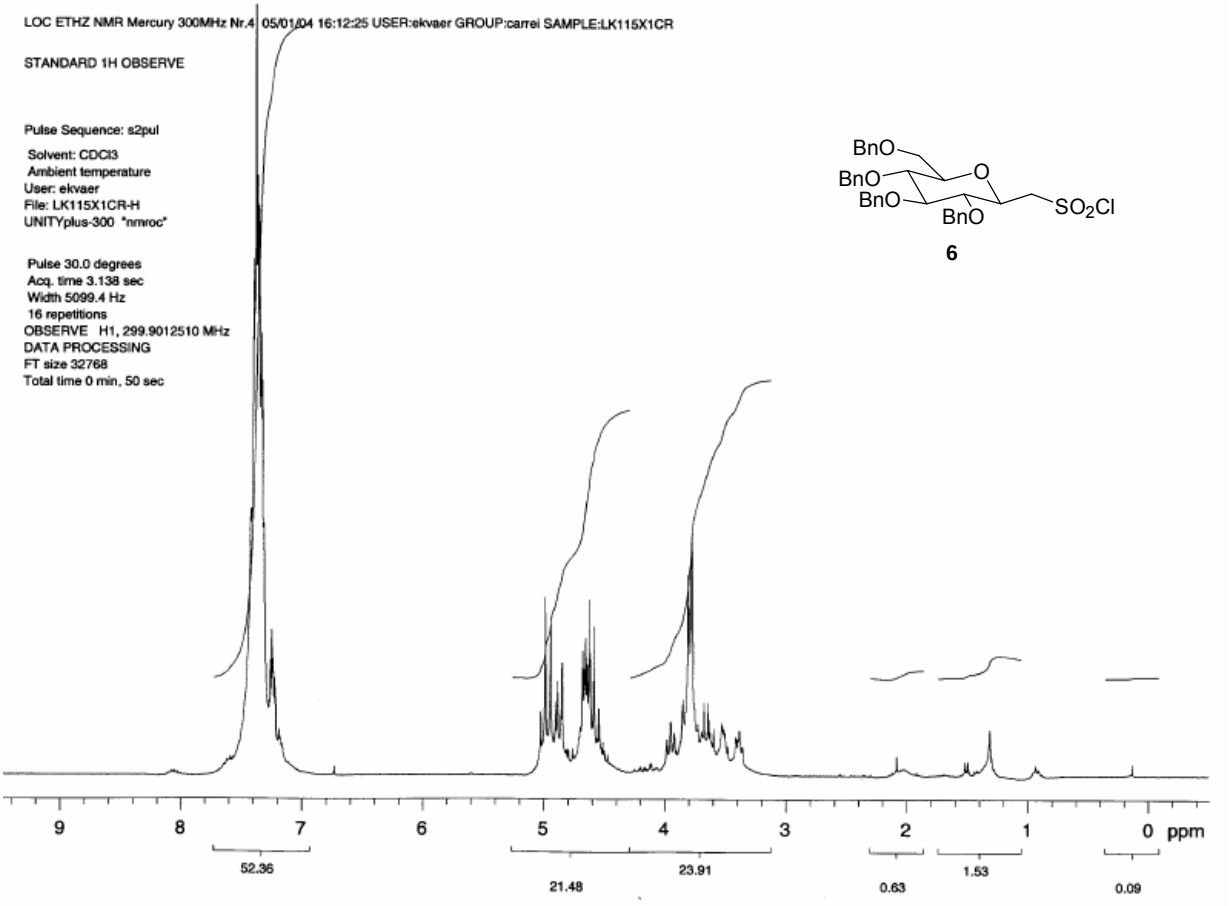

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:10:20 USER:ekvaer GROUP:carrei SAMPLE:LK112X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK112X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
128 repetitions
OBSERVE C13, 75.4102323 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 4 min, 55 sec
BnO
BnO
BnO
O
BnO
OMs
4A
220
200
180
160
140
120
100
80
60
40
20
ppm


LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:11:09 USER:ekvaer GROUP:carrei SAMPLE:LK113X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK113X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
BnO
BnO
BnO
O
SAc
5
9 8 7 6 5 4 3 2 1 0 ppm
48.85
9.69
10.72
20.22
2.52
6.96
0.74
0.41
-0.11

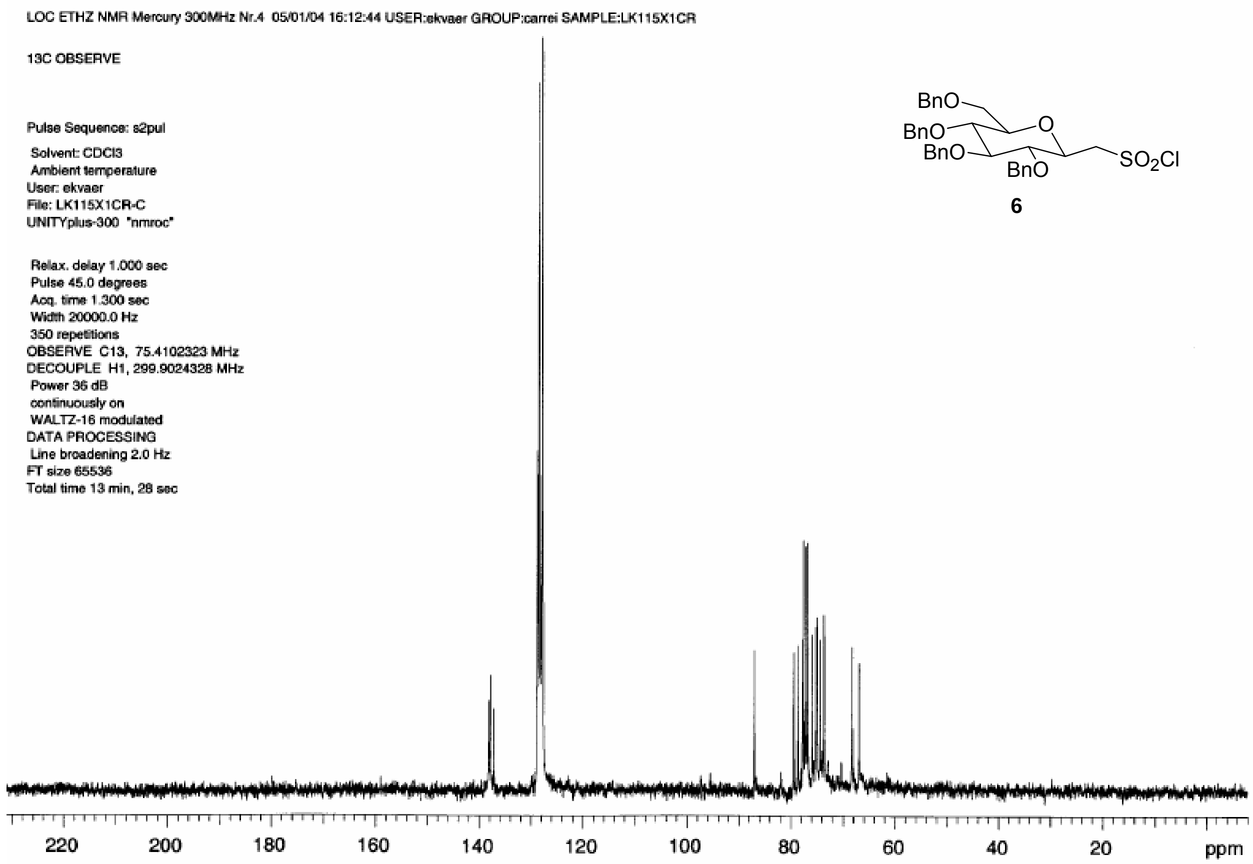

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:11:31 USER:ekvaer GROUP:carrei SAMPLE:LK113X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK113X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
64 repetitions
OBSERVE C13, 75.4102323 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 2 min, 27 sec
BnO
BnO
BnO
BnO
O
SAc
5
220 200 180 160 140 120 100 80 60 40 20 ppm

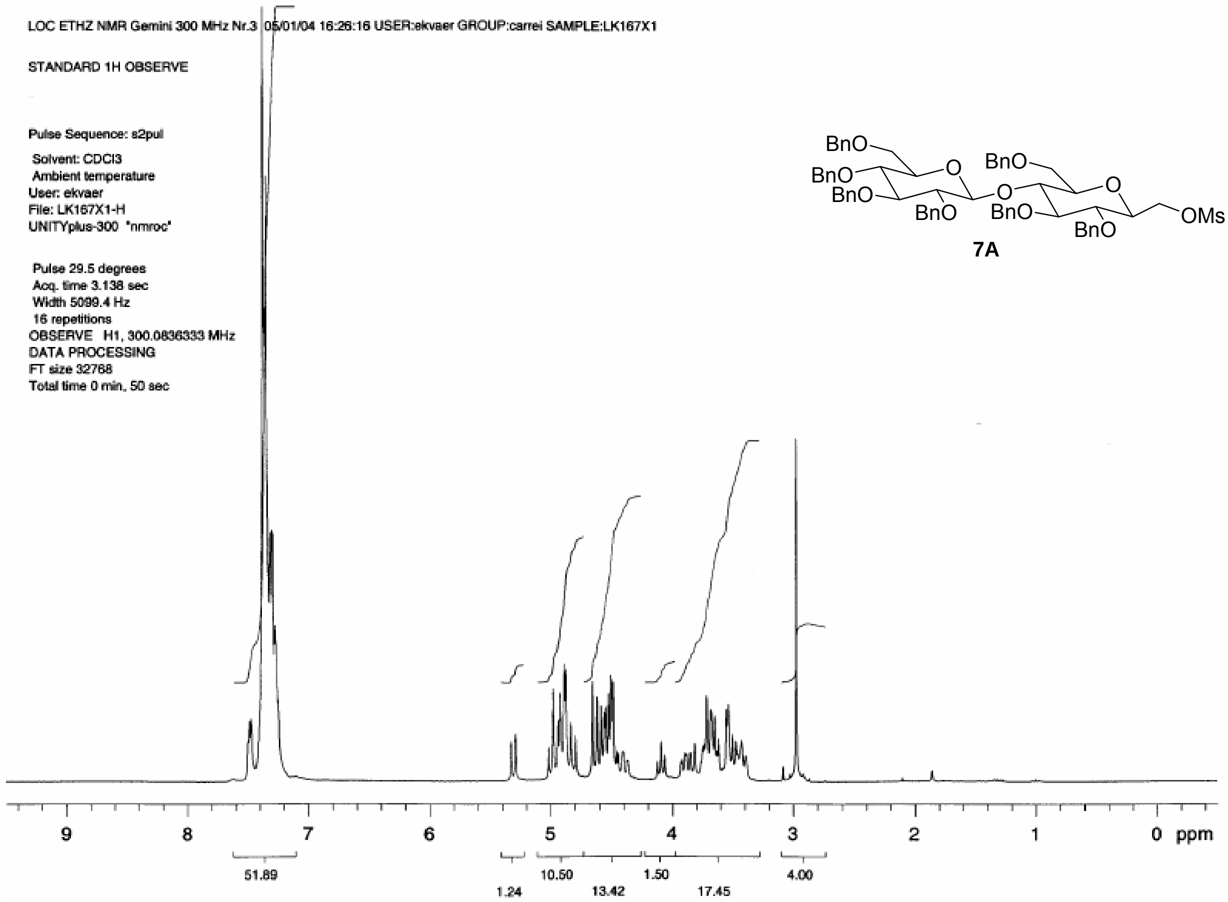

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:12:04 USER:ekvaer GROUP:carrei SAMPLE:LK114X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CD3OD
Ambient temperature
User: ekvaer
File: LK114X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9024335 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
BnO
BnO
BnO
O
SO3Na
9 8 7 6 5 4 3 2 1 0 ppm
2.42
4.95
39.38
26.66
21.15
3.65
1.79

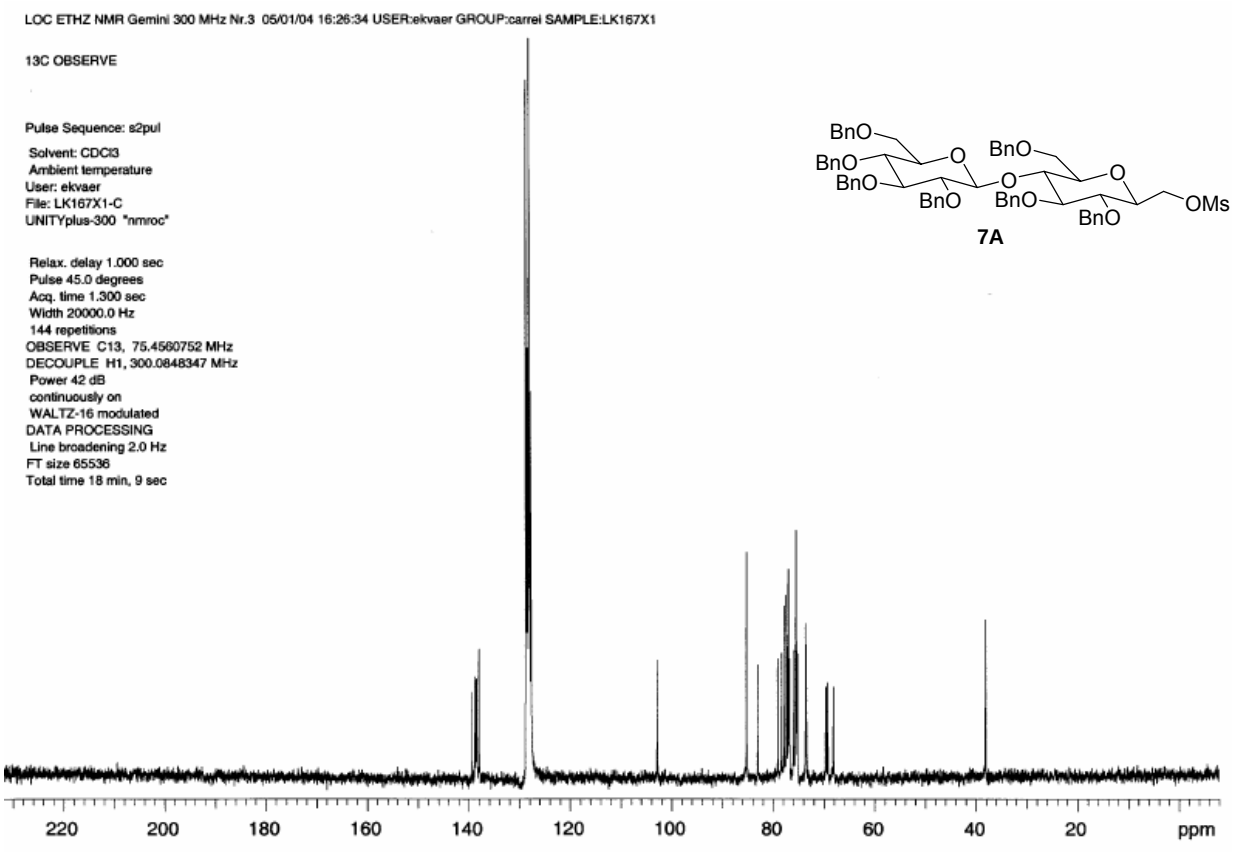
5A


LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:12:25 USER:ekvaer GROUP:carrei SAMPLE:LK115X1CR
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK115X1CR-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
BnO
BnO
BnO
O
SO2Cl
9 8 7 6 5 4 3 2 1 0 ppm
52.36
21.48
23.91
0.63
1.53
0.09

6

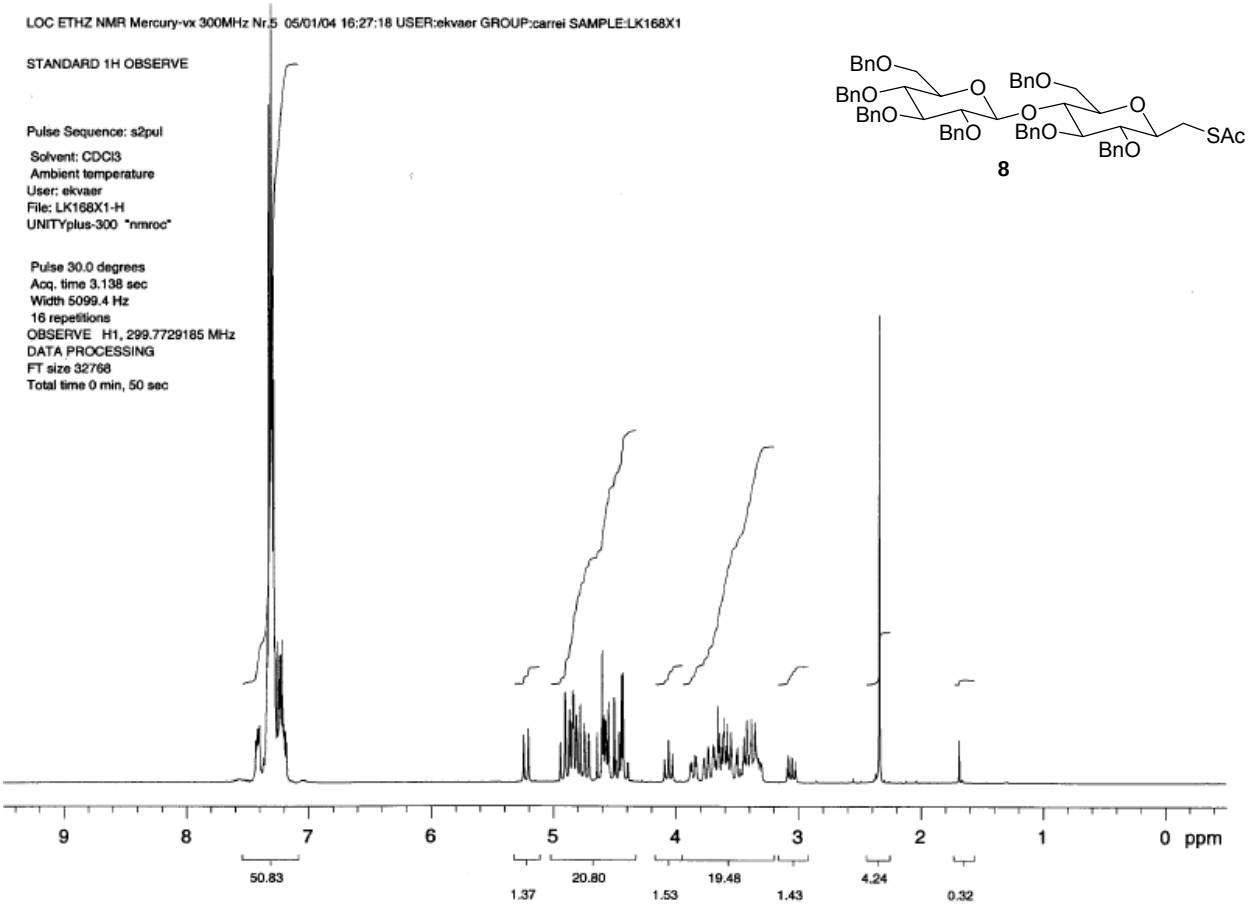

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:12:44 USER:ekvaer GROUP:carrei SAMPLE:LK115X1CR
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK115X1CR-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
350 repetitions
OBSERVE C13, 75.4102323 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 13 min, 28 sec
BnO
BnO
BnO
BnO
O
SO2Cl
6
220 200 180 160 140 120 100 80 60 40 20 ppm


LOC ETHZ NMR Gemini 300 MHz Nr.3 05/01/04 16:26:16 USER:ekvaer GROUP:carrei SAMPLE:LK167X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK167X1-H
UNITYplus-300 "nmroc"
Pulse 29.5 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.0836333 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
BnO
BnO
BnO
O
BnO
O
BnO
BnO
O
OMs
7A
9 8 7 6 5 4 3 2 1 0 ppm
51.89
1.24
10.50
13.42
1.50
17.45
4.00


LOC ETHZ NMR Gemini 300 MHz Nr.3 05/01/04 16:26:34 USER:ekvaer GROUP:carrei SAMPLE:LK167X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK167X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
144 repetitions
OBSERVE C13, 75.4560752 MHz
DECOUPLE H1, 300.0848347 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 18 min, 9 sec
220
200
180
160
140
120
100
80
60
40
20
ppm

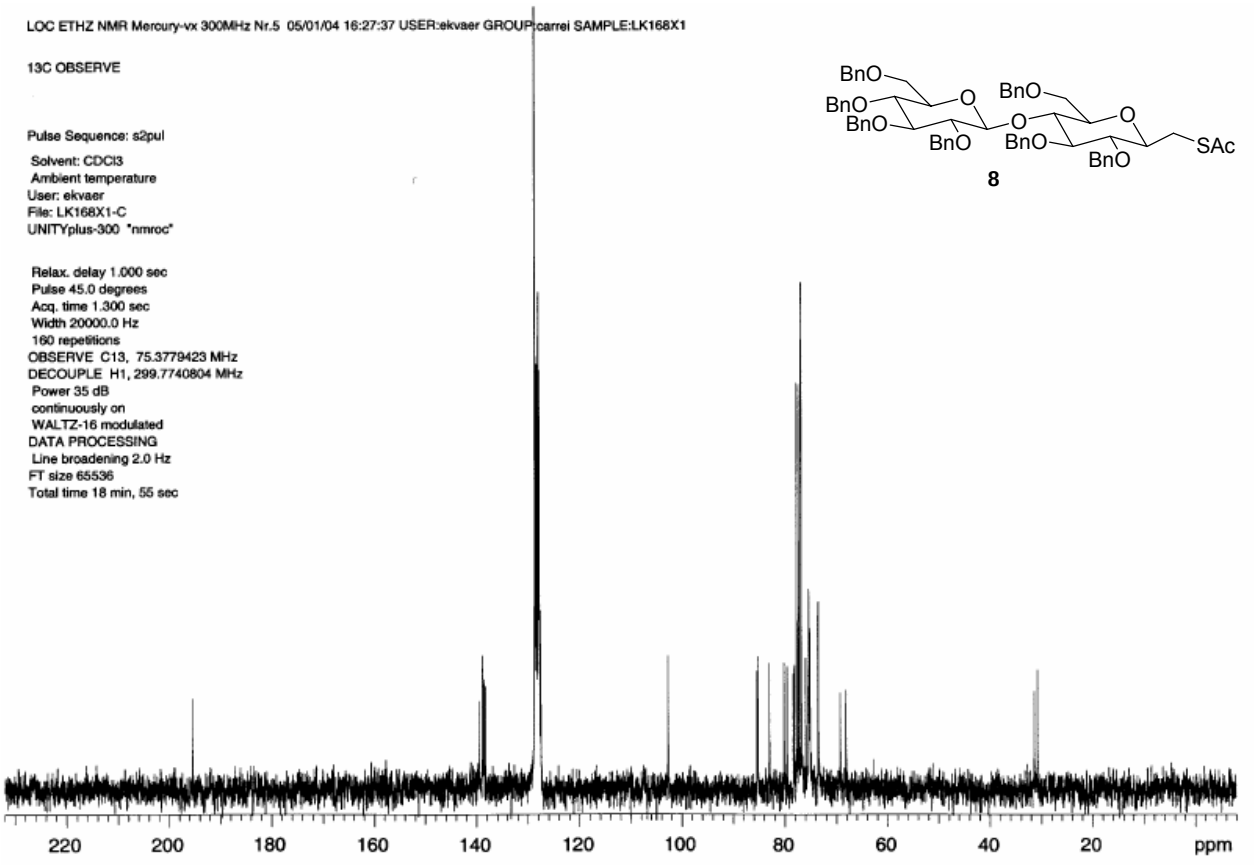
BnO
BnO
BnO
BnO
O
BnO
O
BnO
BnO
O
BnO
OMs

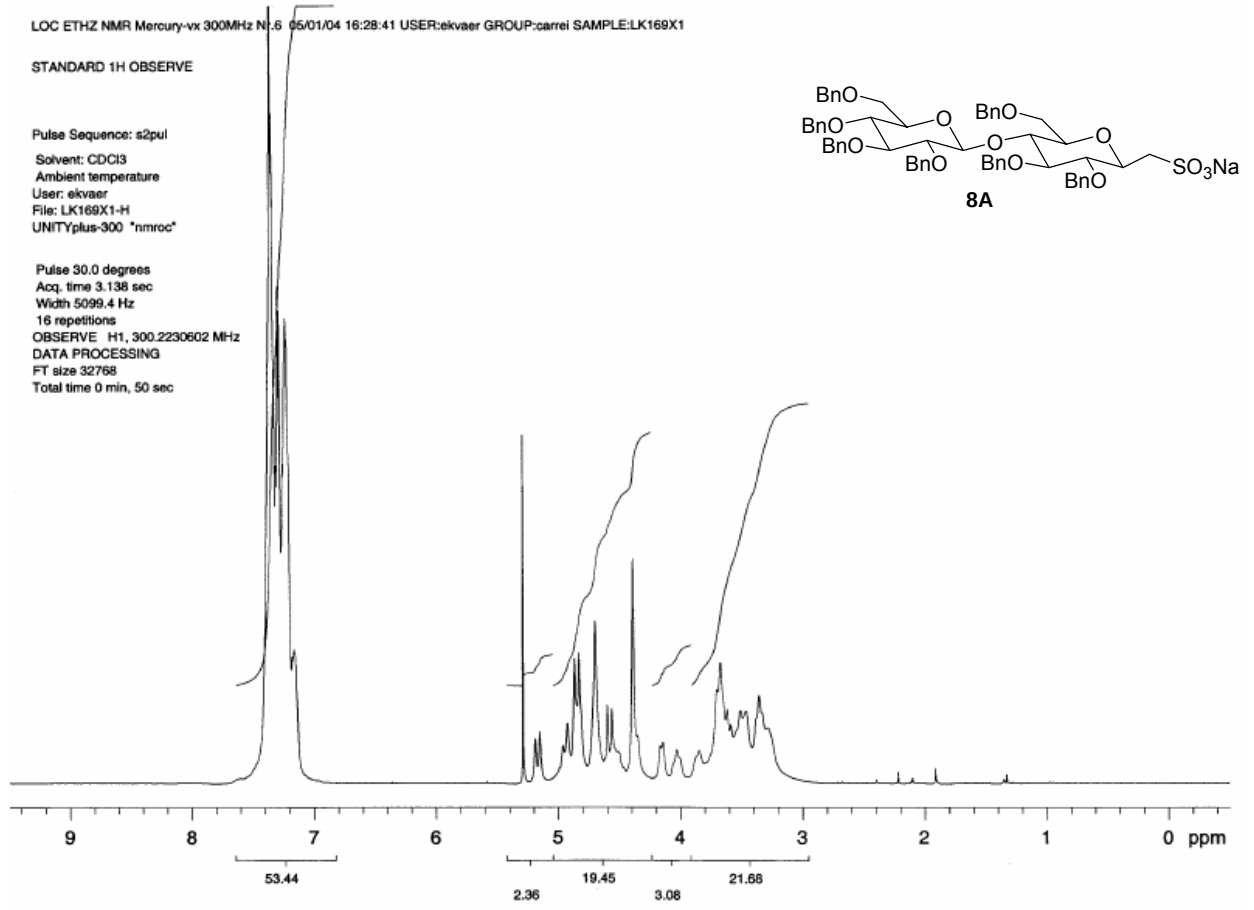
7A

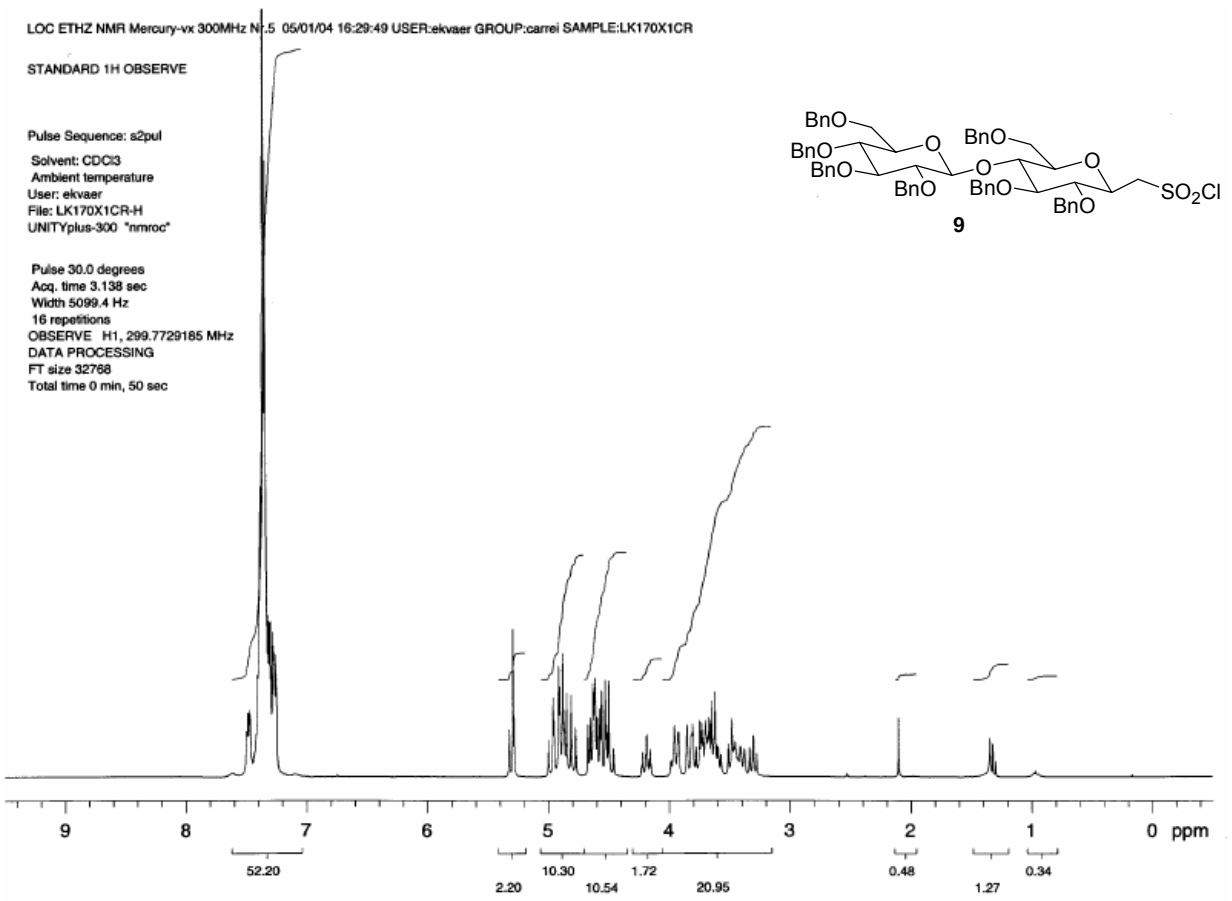

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 16:27:18 USER:ekvaer GROUP:carrei SAMPLE:LK168X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK168X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.7729185 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
9
8
7
6
5
4
3
2
1
0 ppm
50.83
1.37
20.80
1.53
19.48
1.43
4.24
0.32

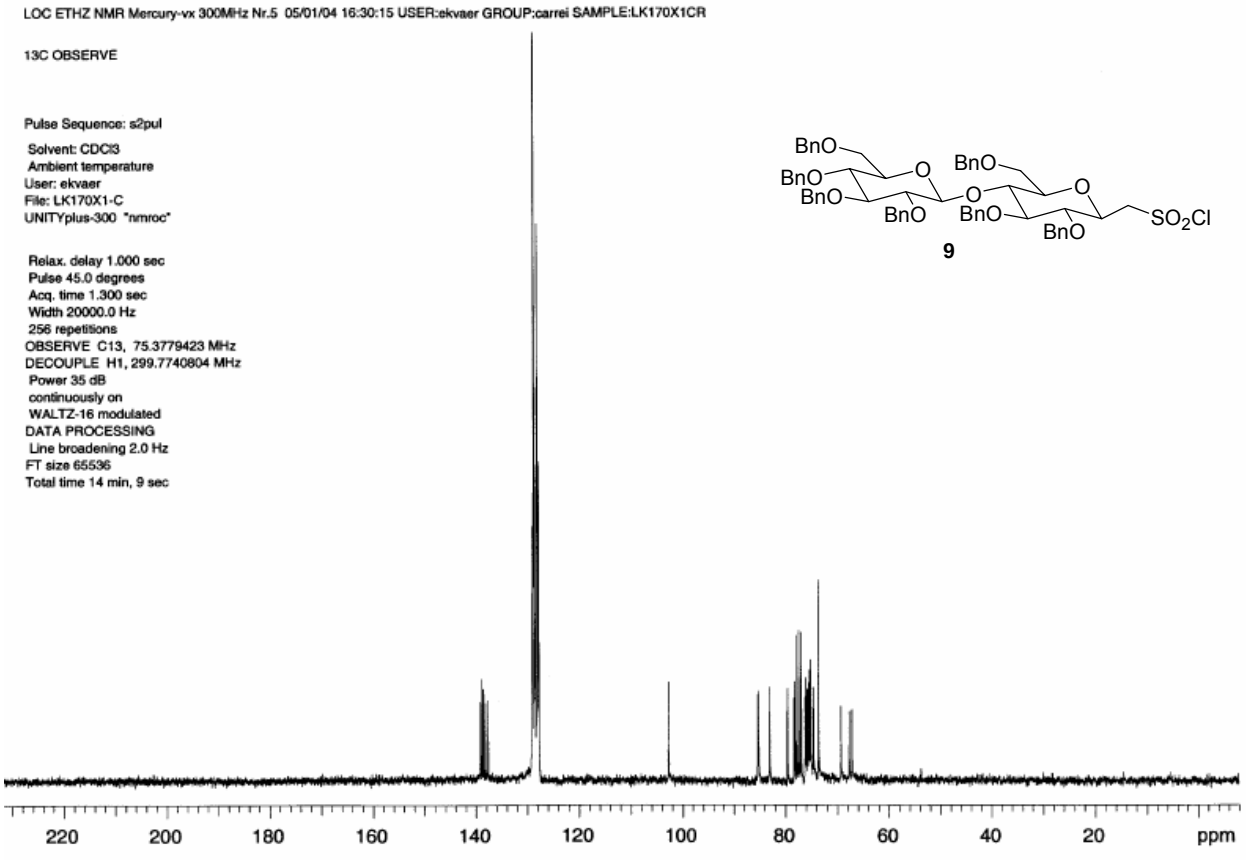
BnO
BnO
BnO
BnO
O
BnO
O
BnO
BnO
O
BnO
SAc

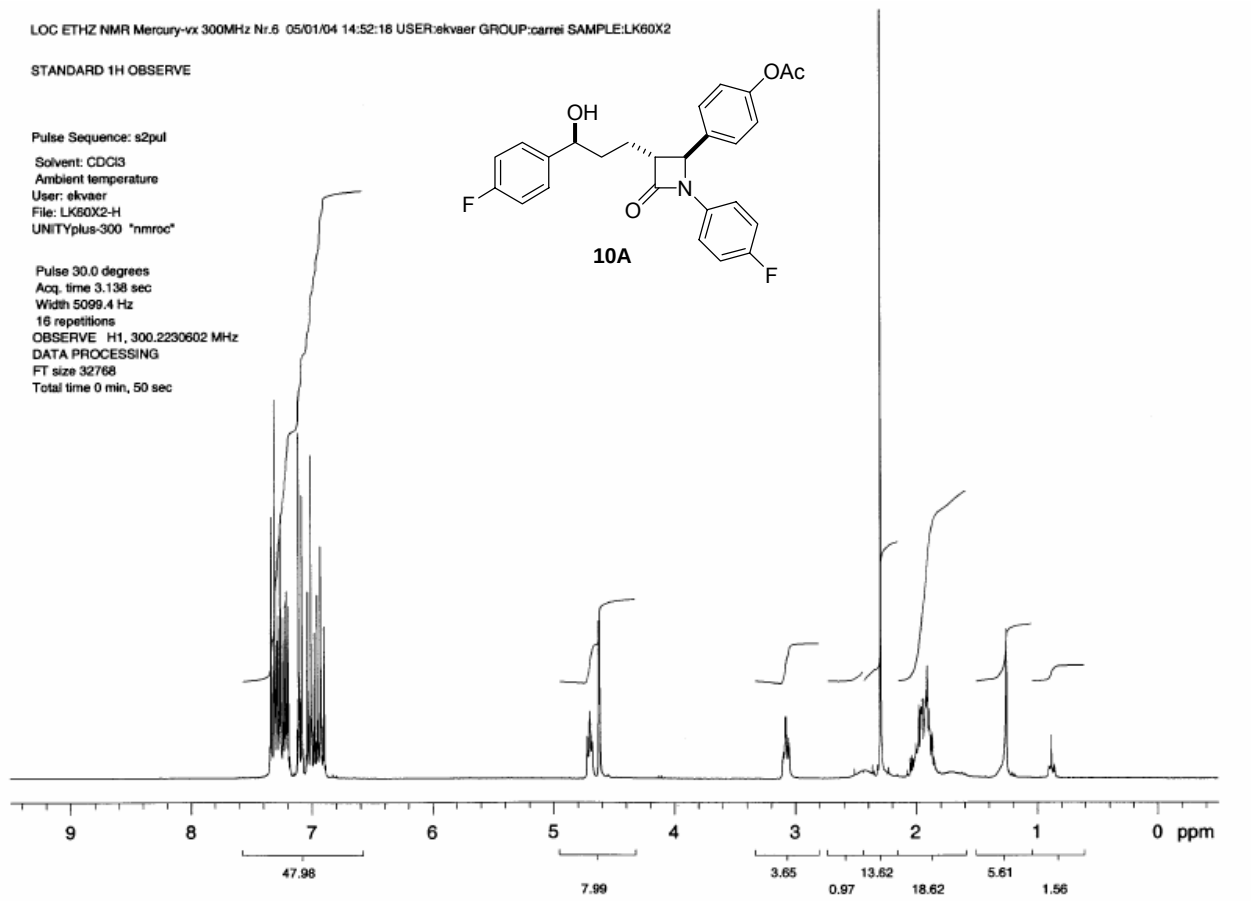
8

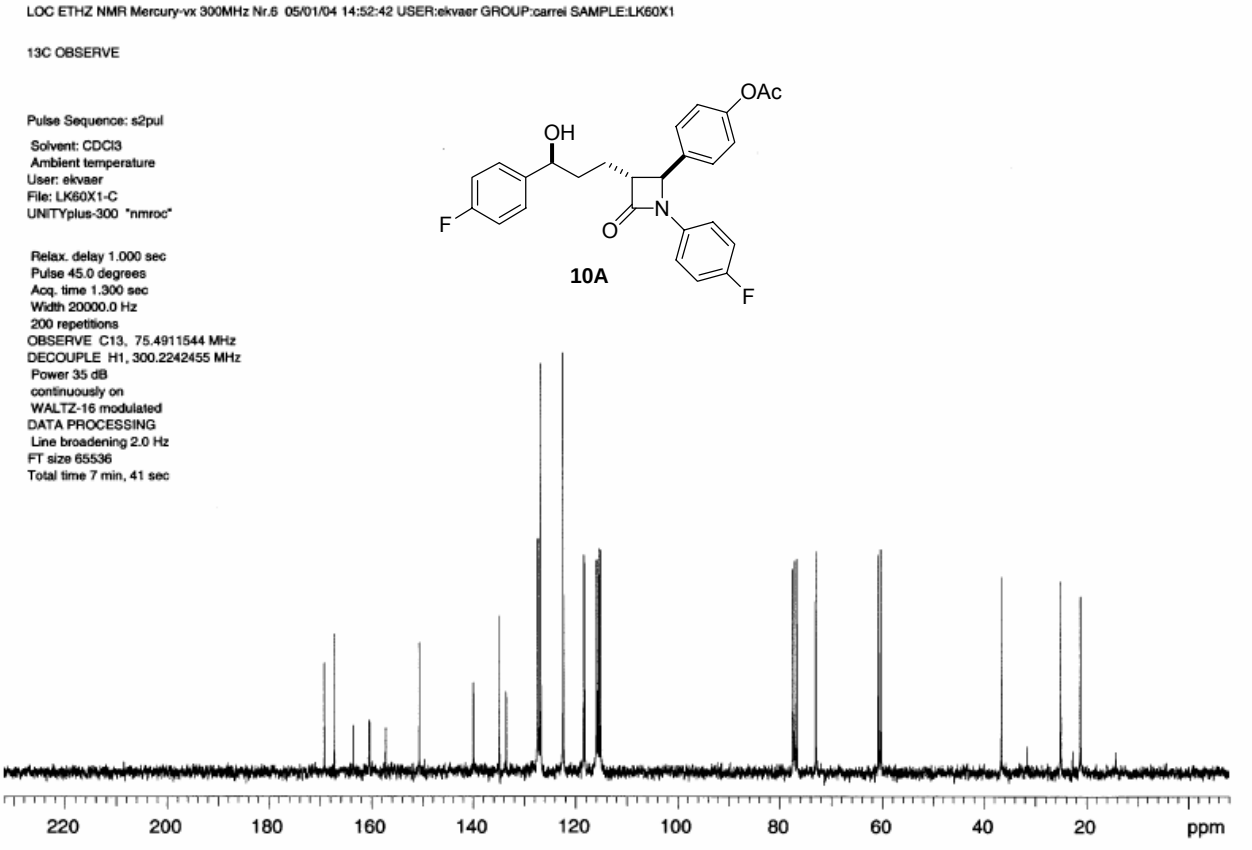

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 16:27:37 USER:ekvaer GROUP:carrei SAMPLE:LK168X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK168X1-C
UNITYplus-300 *nmroc*
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
160 repetitions
OBSERVE C13, 75.3779423 MHz
DECOUPLE H1, 299.7740804 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 18 min, 55 sec
BnO
O
SAc
8
220
200
180
160
140
120
100
80
60
40
20
ppm

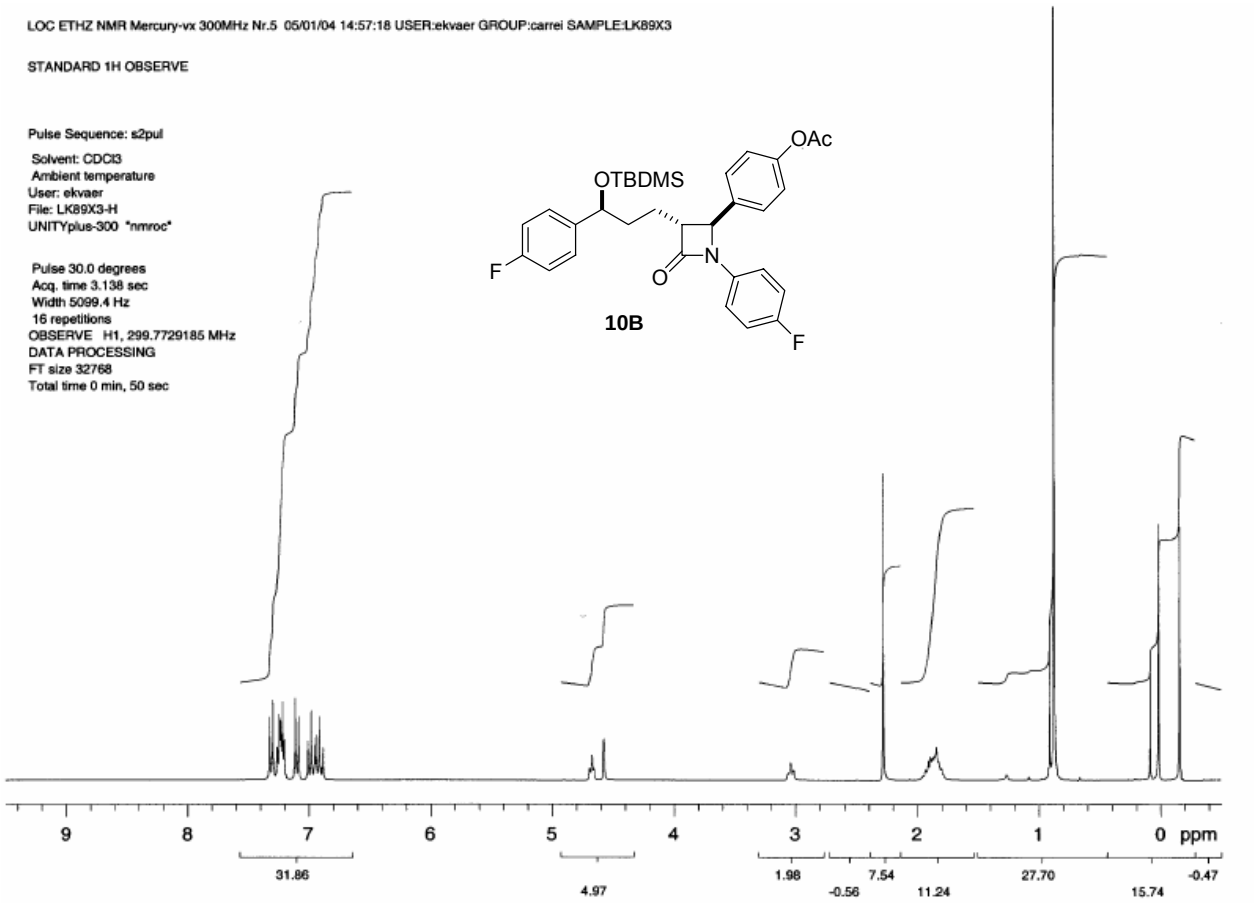

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:28:41 USER:ekvaer GROUP:carrei SAMPLE:LK169X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK169X1-H
UNITYplus-300 *nmroc*
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
O
SO3Na
8A
9
8
7
6
5
4
3
2
1
0 ppm
53.44
2.36
19.45
3.08
21.68

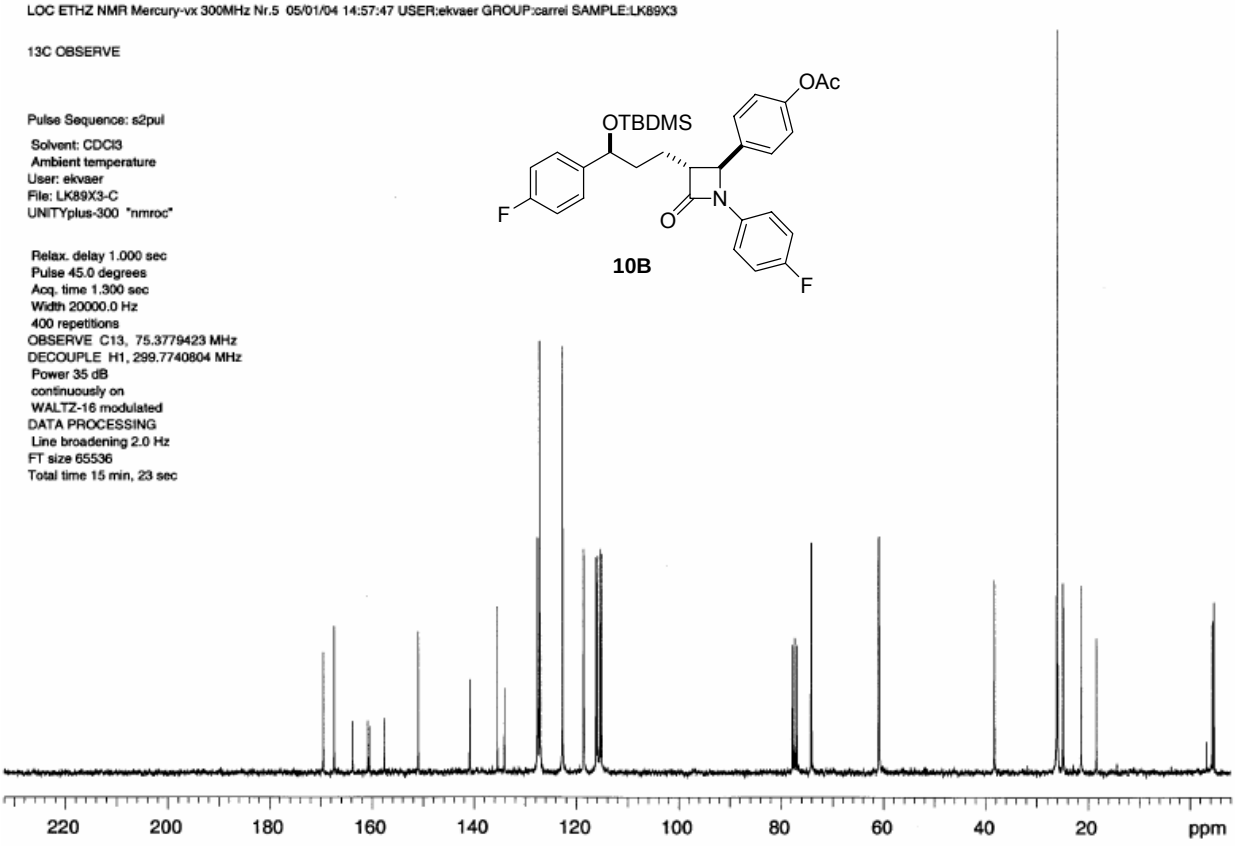

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 16:29:49 USER:ekvaer GROUP:carrei SAMPLE:LK170X1CR
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK170X1CR-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.7729185 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
BnO
O
SO2Cl
9
9 8 7 6 5 4 3 2 1 0 ppm
52.20
2.20
10.30
10.54
1.72
20.95
0.48
1.27
0.34

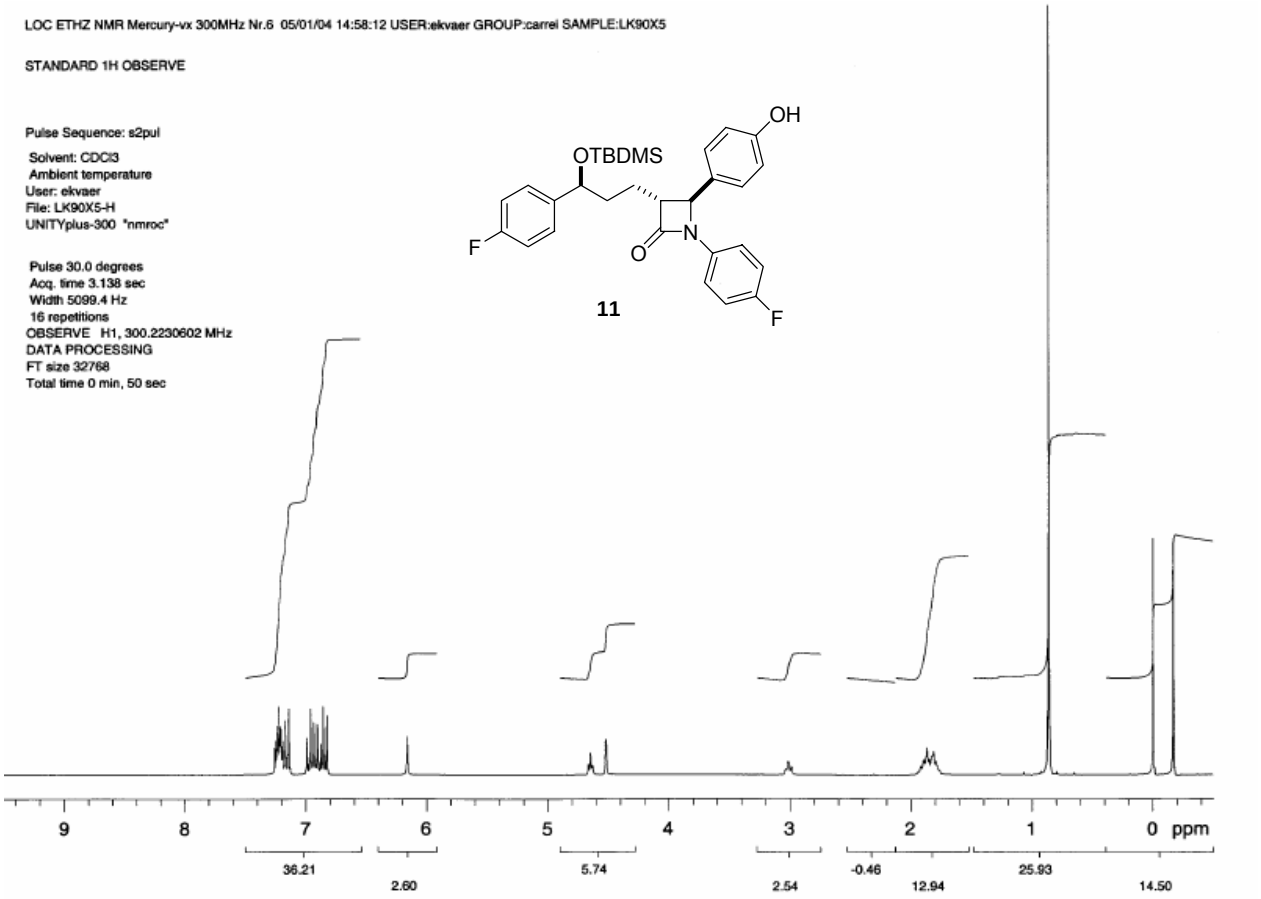

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 16:30:15 USER:ekvaer GROUP:carrei SAMPLE:LK170X1CR
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK170X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
256 repetitions
OBSERVE C13, 75.3779423 MHz
DECOUPLE H1, 299.7740804 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 14 min, 9 sec
BnO
O
SO2Cl
9
220 200 180 160 140 120 100 80 60 40 20 ppm

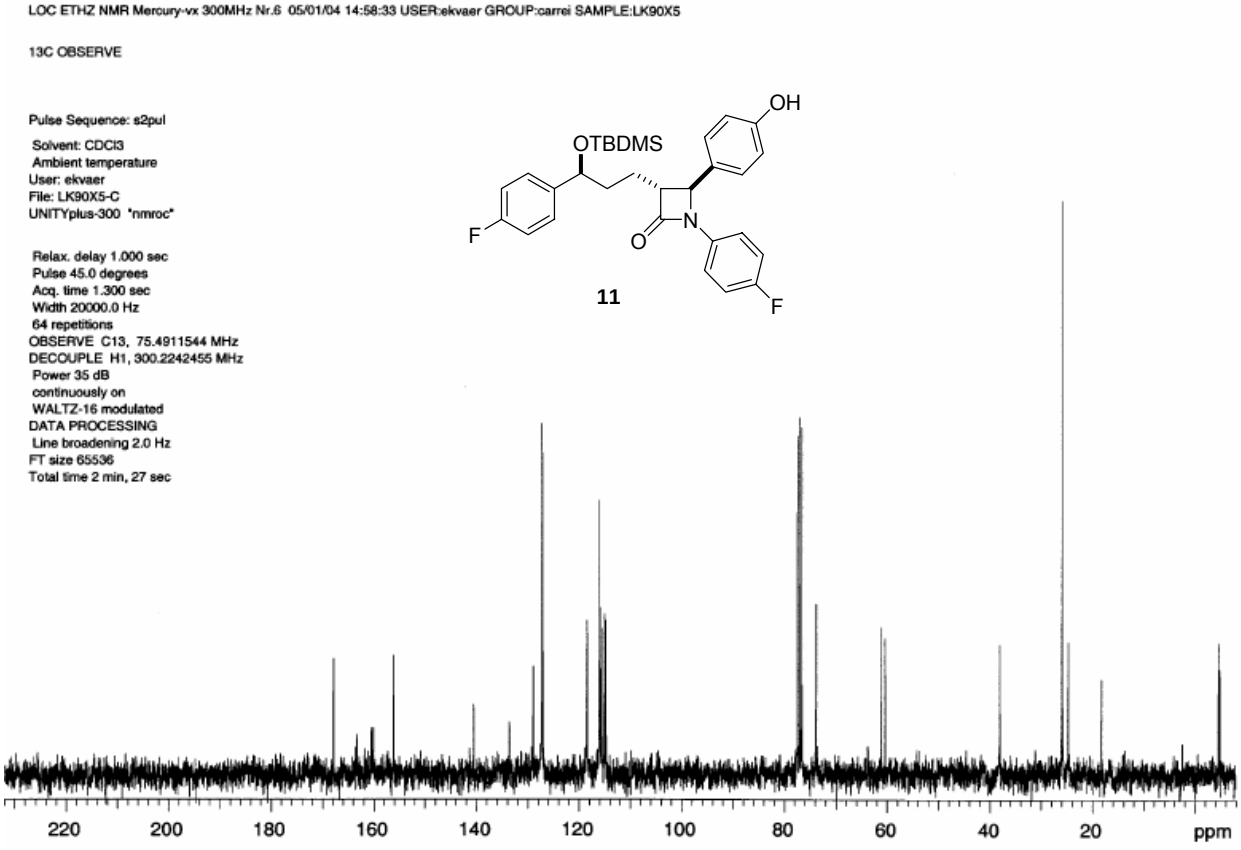

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 14:52:18 USER:ekvaer GROUP:carrei SAMPLE:LK60X2
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK60X2-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OAc
OH
F
N
O
F
10A
9
8
7
6
5
4
3
2
1
0 ppm
47.98
7.99
3.65
0.97
13.62
18.62
5.61
1.56

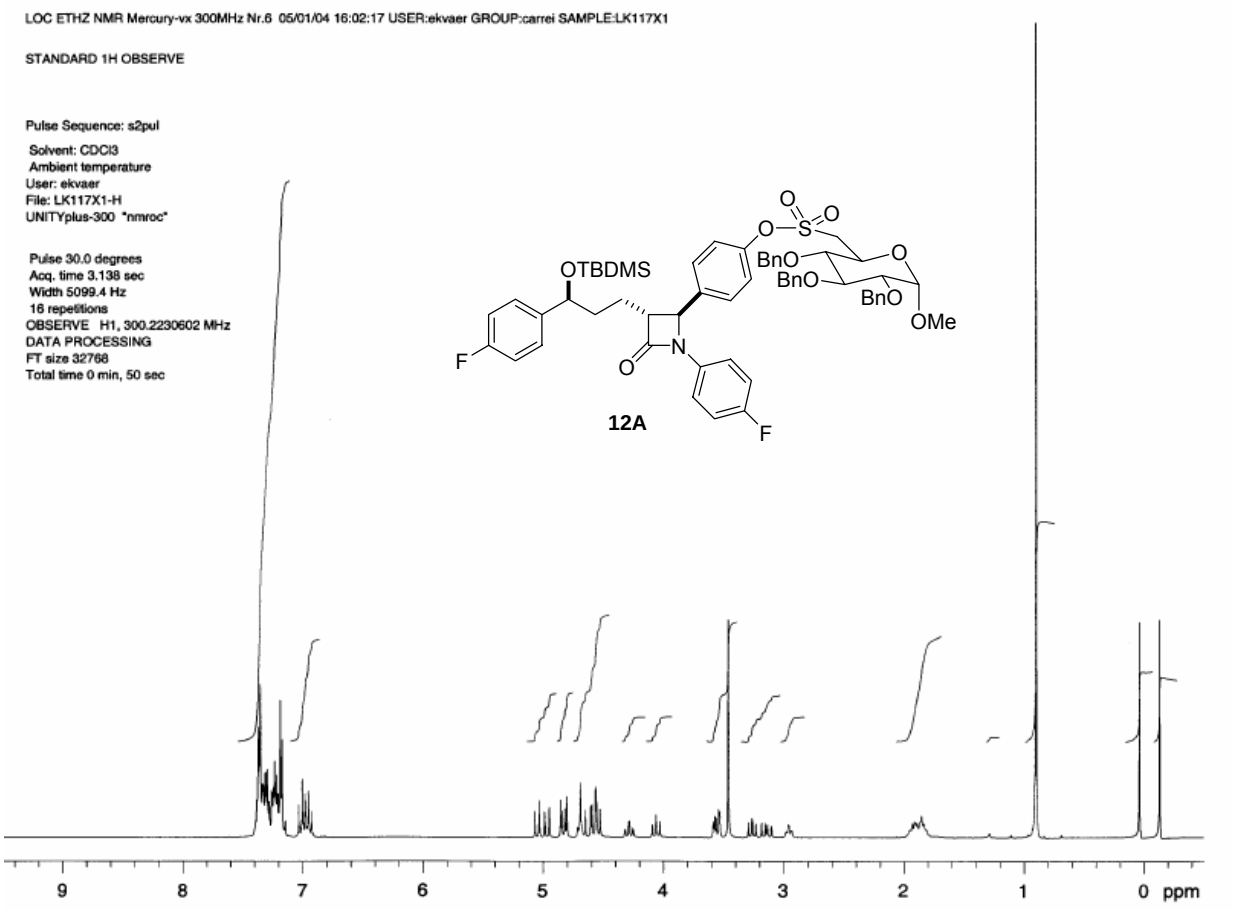

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 14:52:42 USER:ekvaer GROUP:carrei SAMPLE:LK60X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK60X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
200 repetitions
OBSERVE C13, 75.4911544 MHz
DECOUPLE H1, 300.2242455 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 7 min, 41 sec
OAc
OH
F
N
O
F
10A
220
200
180
160
140
120
100
80
60
40
20
ppm

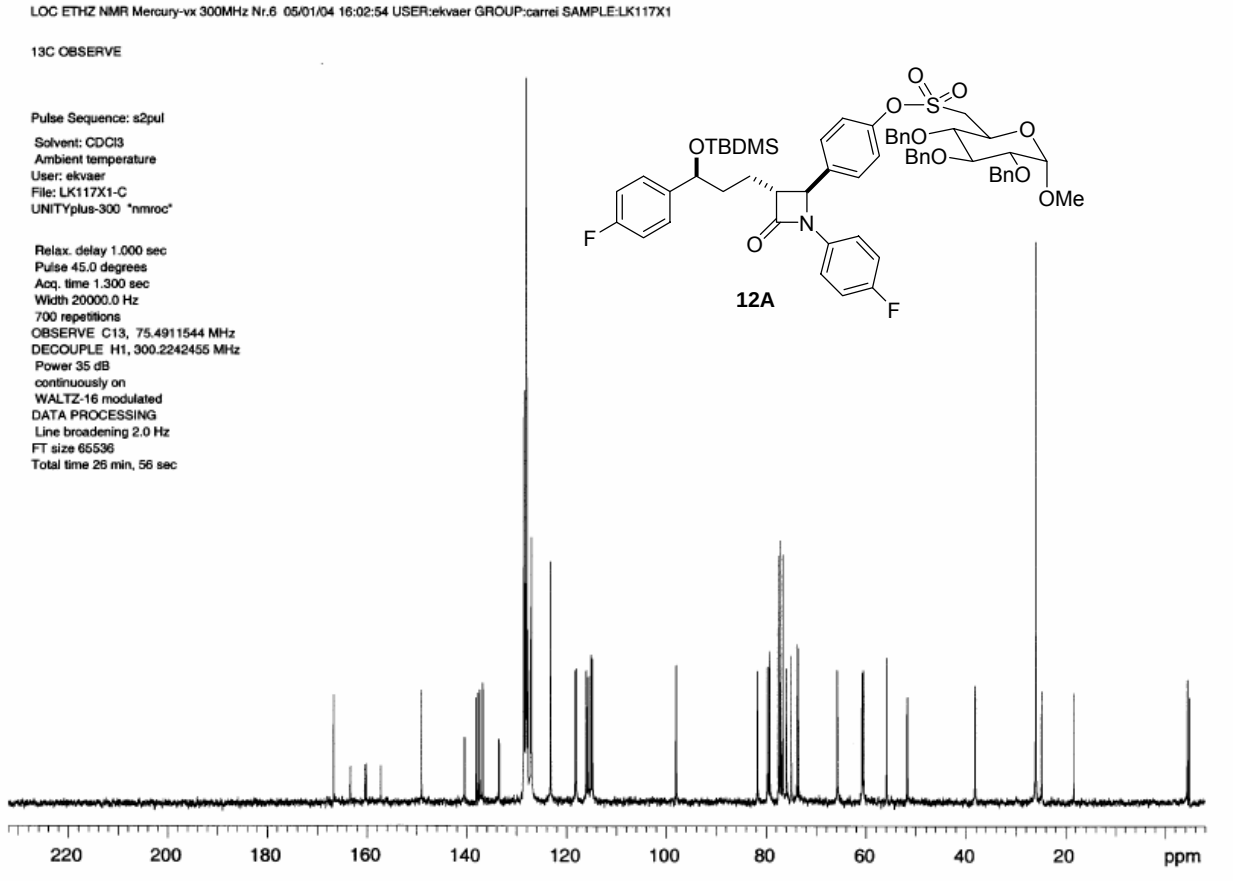

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 14:57:18 USER:ekvaer GROUP:carrei SAMPLE:LK89X3
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK89X3-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.7729185 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OAc
OTBDMS
F
O
N
F
10B
9
8
7
6
5
4
3
2
1
0 ppm
31.86
4.97
1.98
7.54
27.70
-0.47
-0.56
11.24
15.74

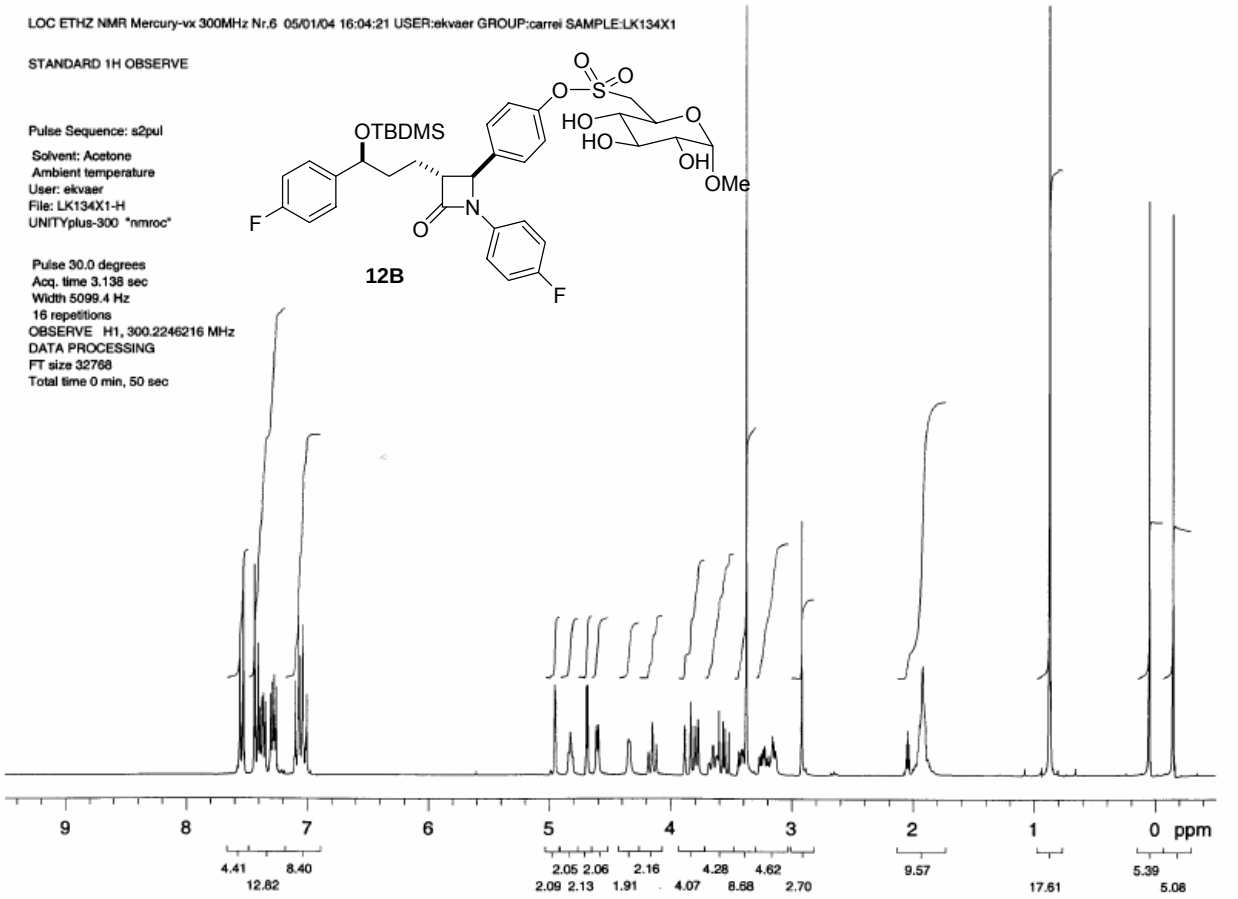

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 14:57:47 USER:ekvaer GROUP:carrei SAMPLE:LK89X3
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK89X3-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
400 repetitions
OBSERVE C13, 75.3779423 MHz
DECOUPLE H1, 299.7740804 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 15 min, 23 sec
OAc
OTBDMS
F
O
N
F
10B
220
200
180
160
140
120
100
80
60
40
20
ppm

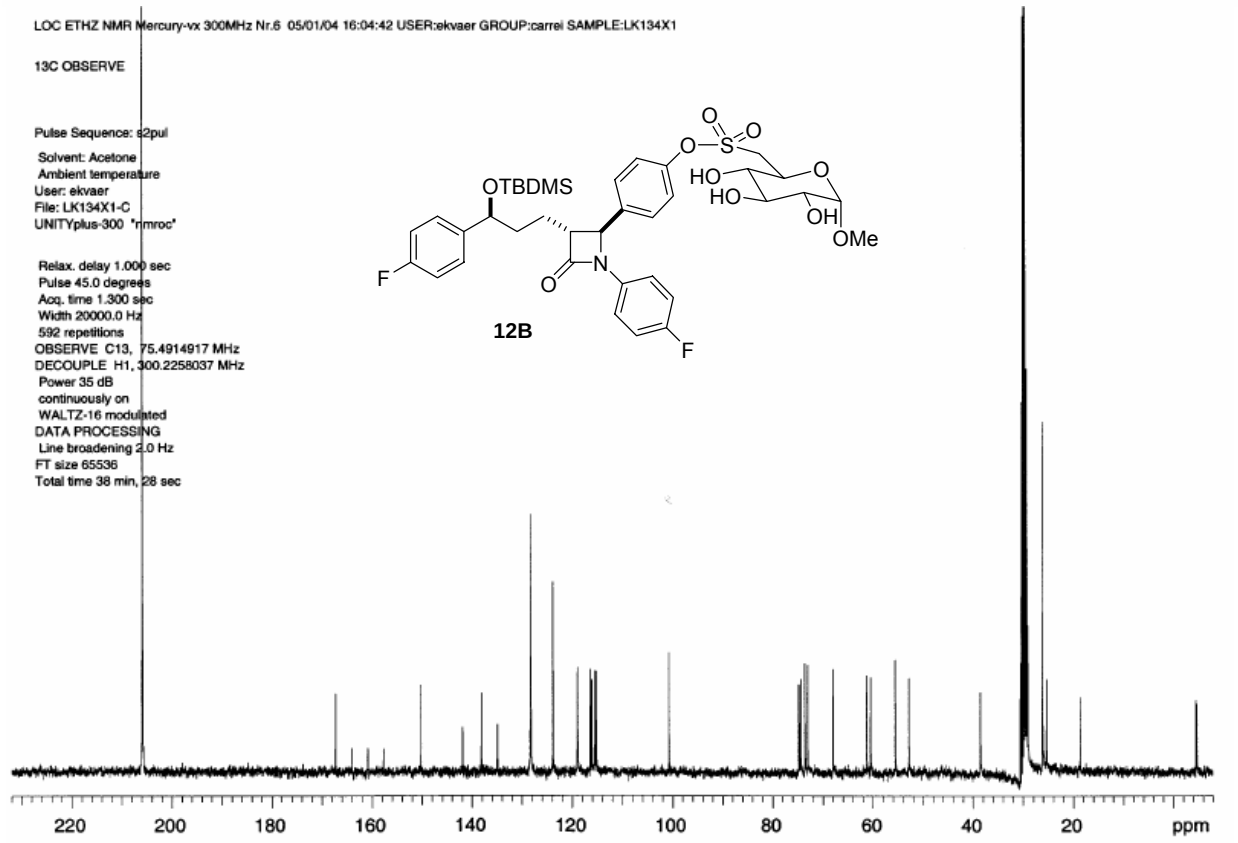

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 14:58:12 USER:ekvaer GROUP:carrei SAMPLE:LK90X5
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK90X5-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OH
OTBDMS
F
O
N
F
11
9
8
7
6
5
4
3
2
1
0 ppm
36.21
2.60
5.74
2.54
-0.46
12.94
25.93
14.50

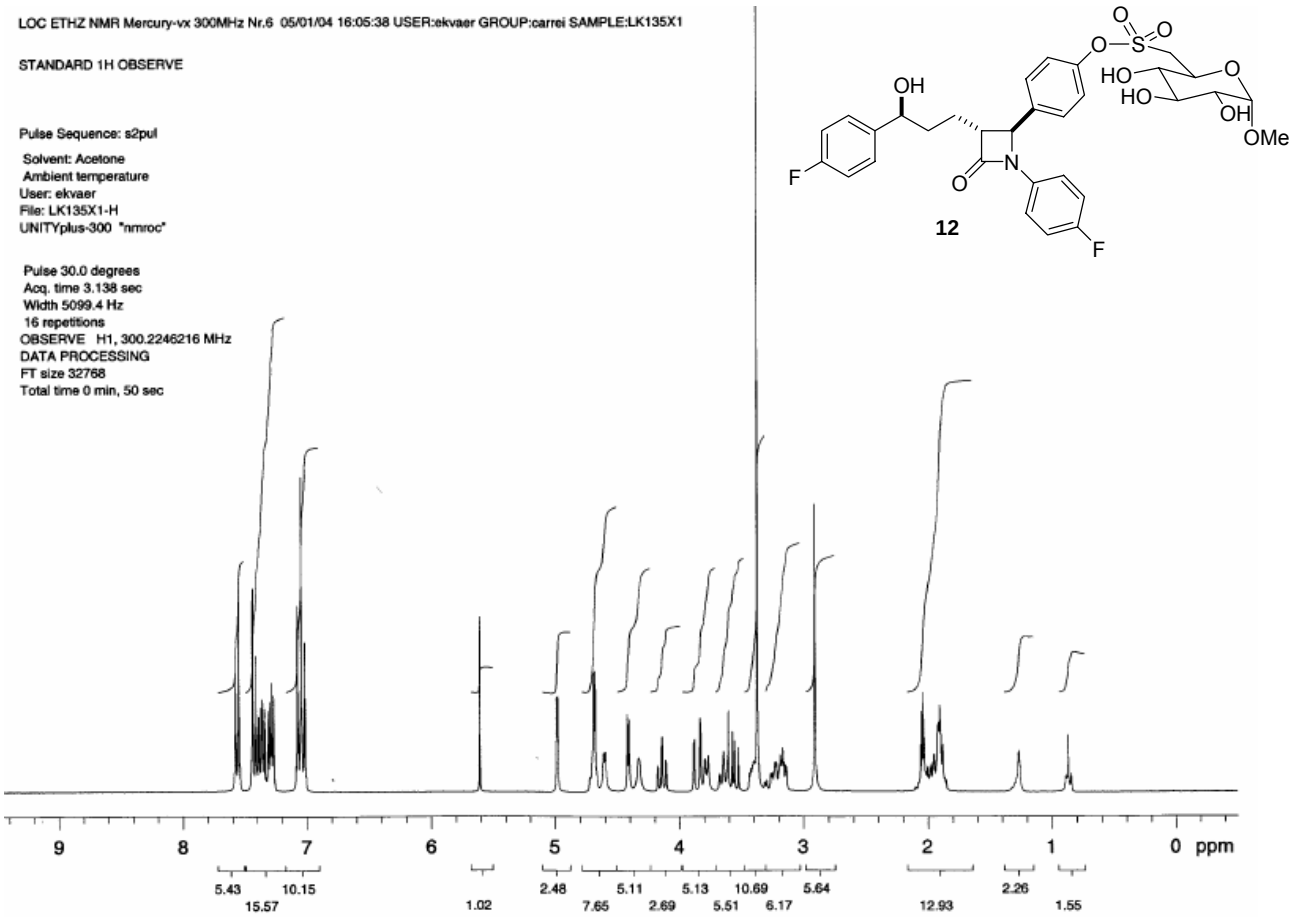

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 14:58:33 USER:ekvaer GROUP:carrei SAMPLE:LK90X5
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK90X5-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
64 repetitions
OBSERVE C13, 75.4911544 MHz
DECOUPLE H1, 300.2242455 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 2 min, 27 sec
OH
OTBDMS
F
O
N
F
11
220
200
180
160
140
120
100
80
60
40
20
ppm

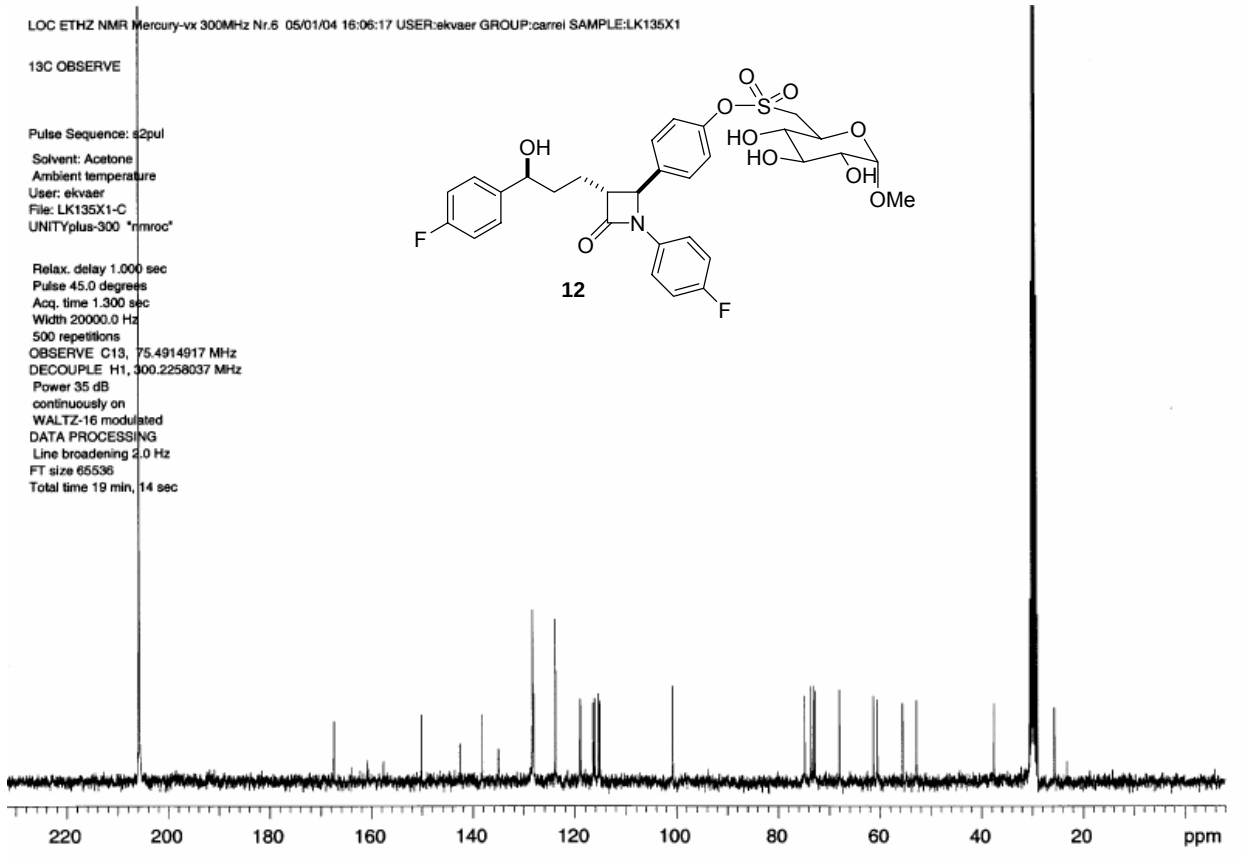

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:02:17 USER:ekvaer GROUP:carrei SAMPLE:LK117X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK117X1-H
UNITYplus-300 *nmroc*
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
BnO
BnO
BnO
OMe
F
F
12A
9
8
7
6
5
4
3
2
1
0 ppm

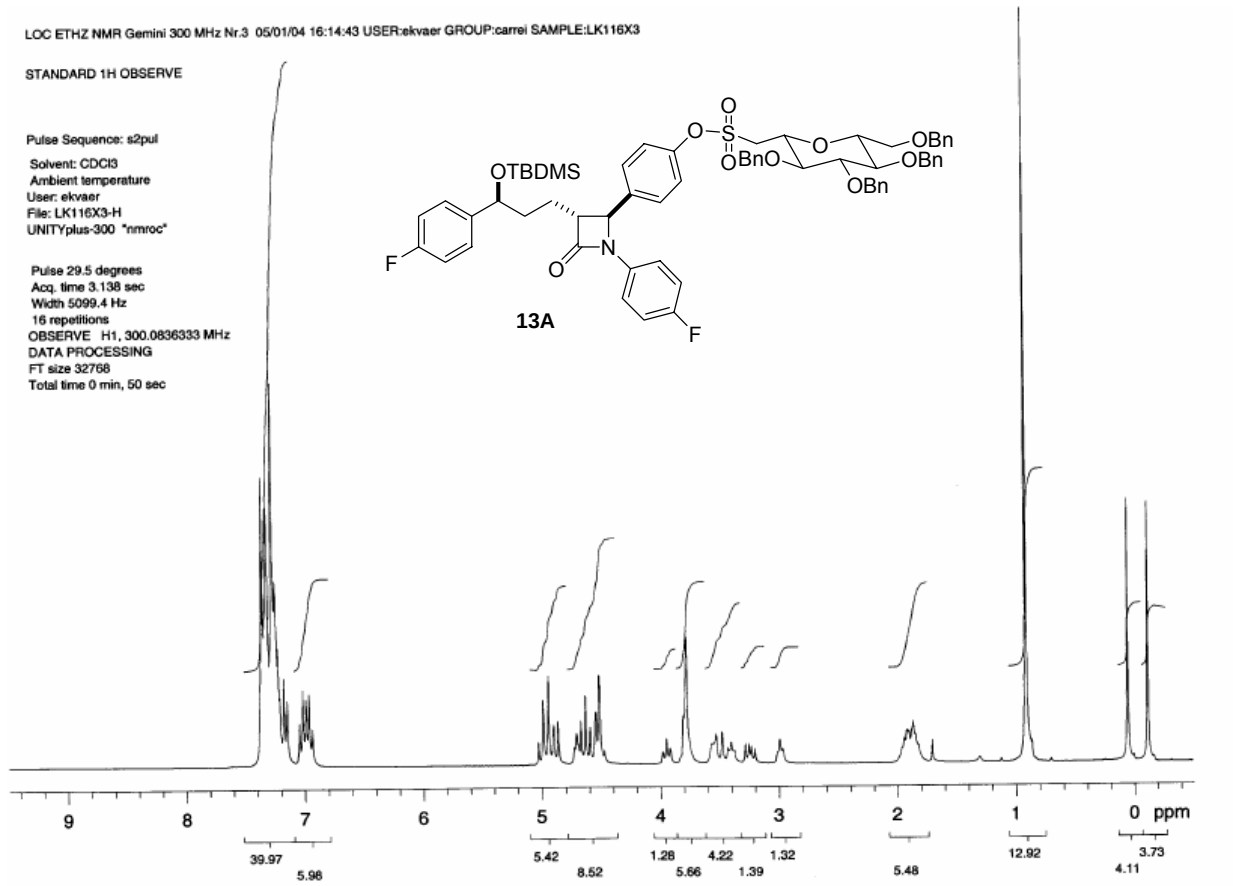

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:02:54 USER:ekvaer GROUP:carrei SAMPLE:LK117X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK117X1-C
UNITYplus-300 *nmroc*
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
700 repetitions
OBSERVE C13, 75.4911544 MHz
DECOUPLE H1, 300.2242455 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 26 min, 56 sec
OTBDMS
BnO
BnO
BnO
OMe
F
F
12A
220
200
180
160
140
120
100
80
60
40
20
ppm

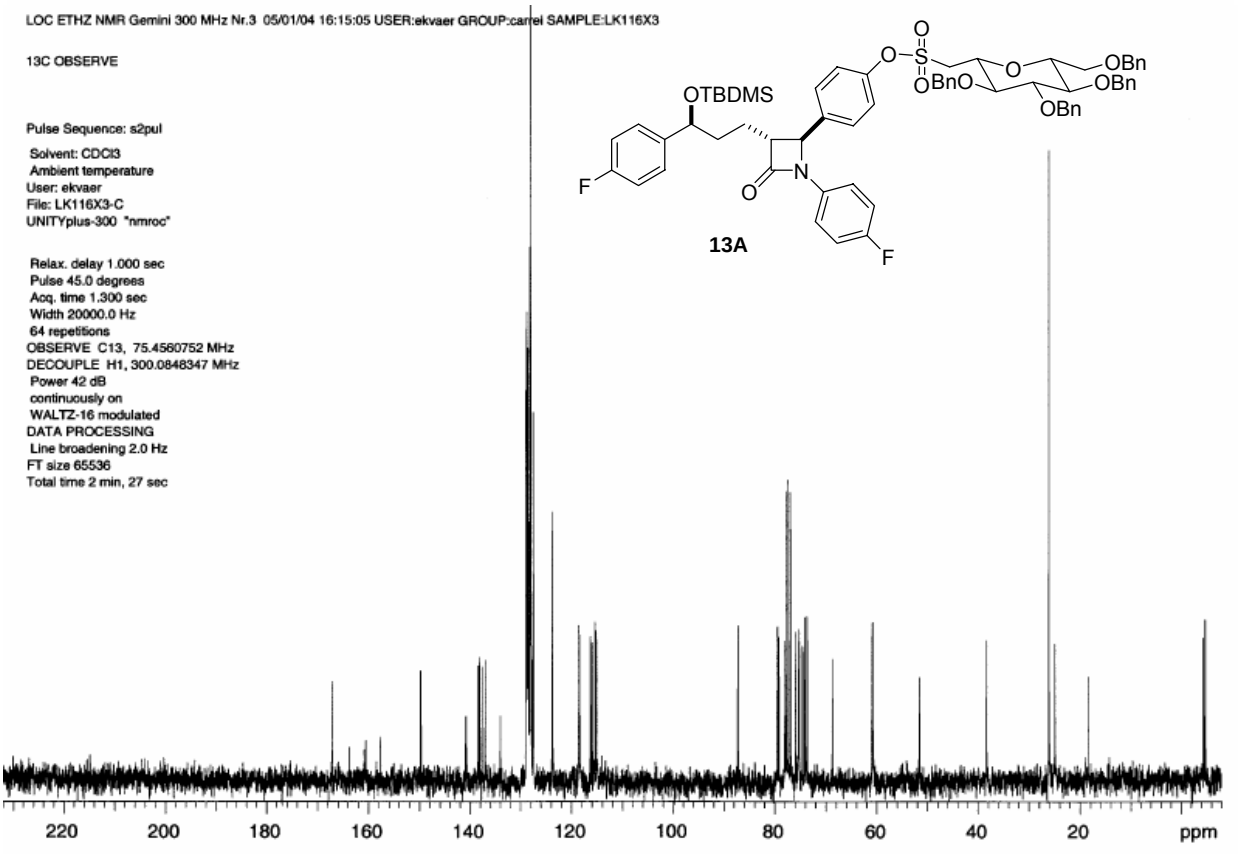

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:04:21 USER:ekvaer GROUP:carrei SAMPLE:LK134X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK134X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2246216 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
HO
HO
OH
OMe
F
N
O
12B
9
8
7
6
5
4
3
2
1
0 ppm
4.41
8.40
12.82
2.05 2.06
2.09 2.13
2.16
1.91
4.28
4.62
4.07
8.68
2.70
9.57
17.61
5.39
5.08

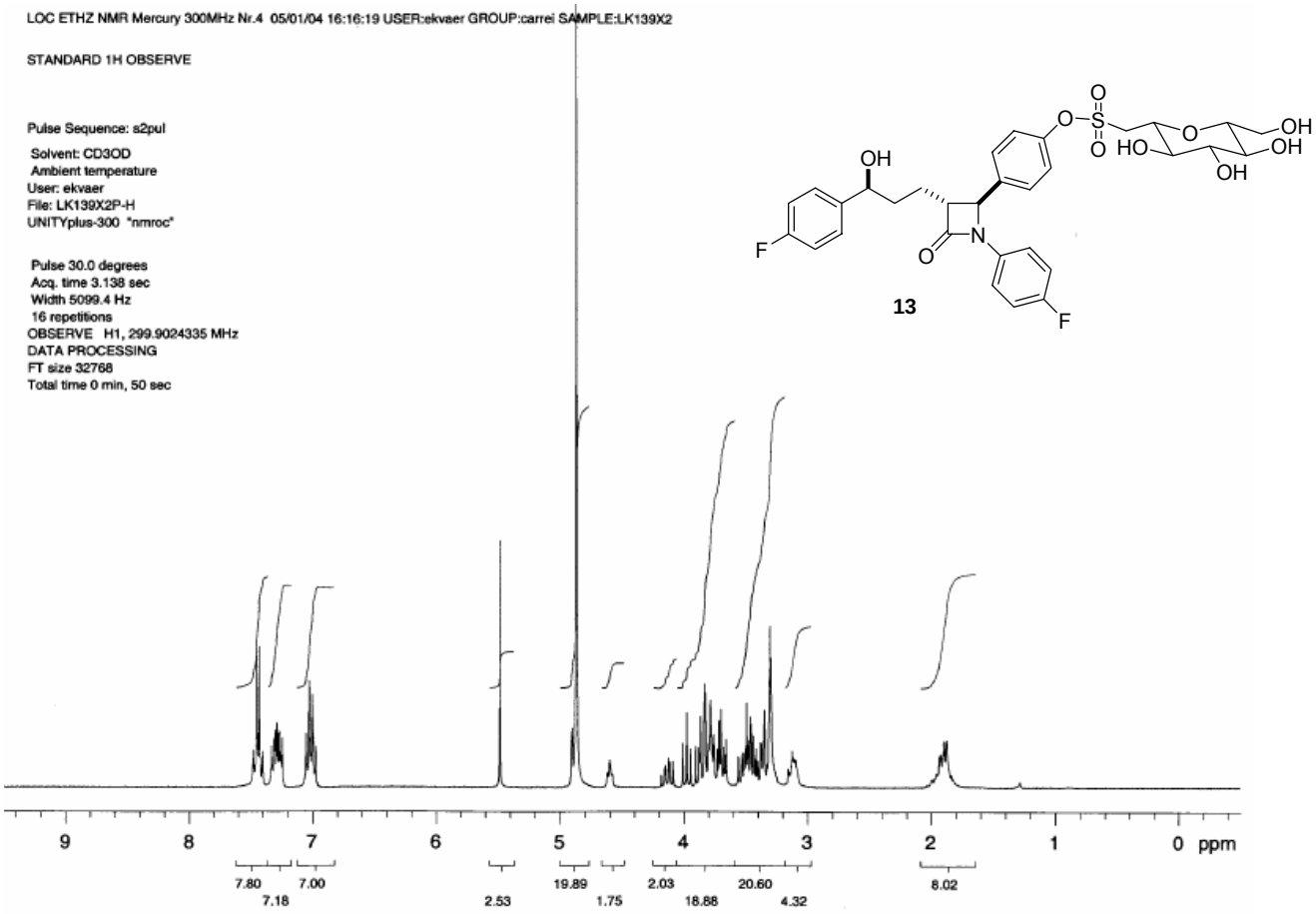

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:04:42 USER:ekvaer GROUP:carrei SAMPLE:LK134X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK134X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
592 repetitions
OBSERVE C13, 75.4914917 MHz
DECOUPLE H1, 300.2258037 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 38 min, 28 sec
OTBDMS
HO
HO
OH
OMe
F
N
O
12B
220
200
180
160
140
120
100
80
60
40
20
ppm

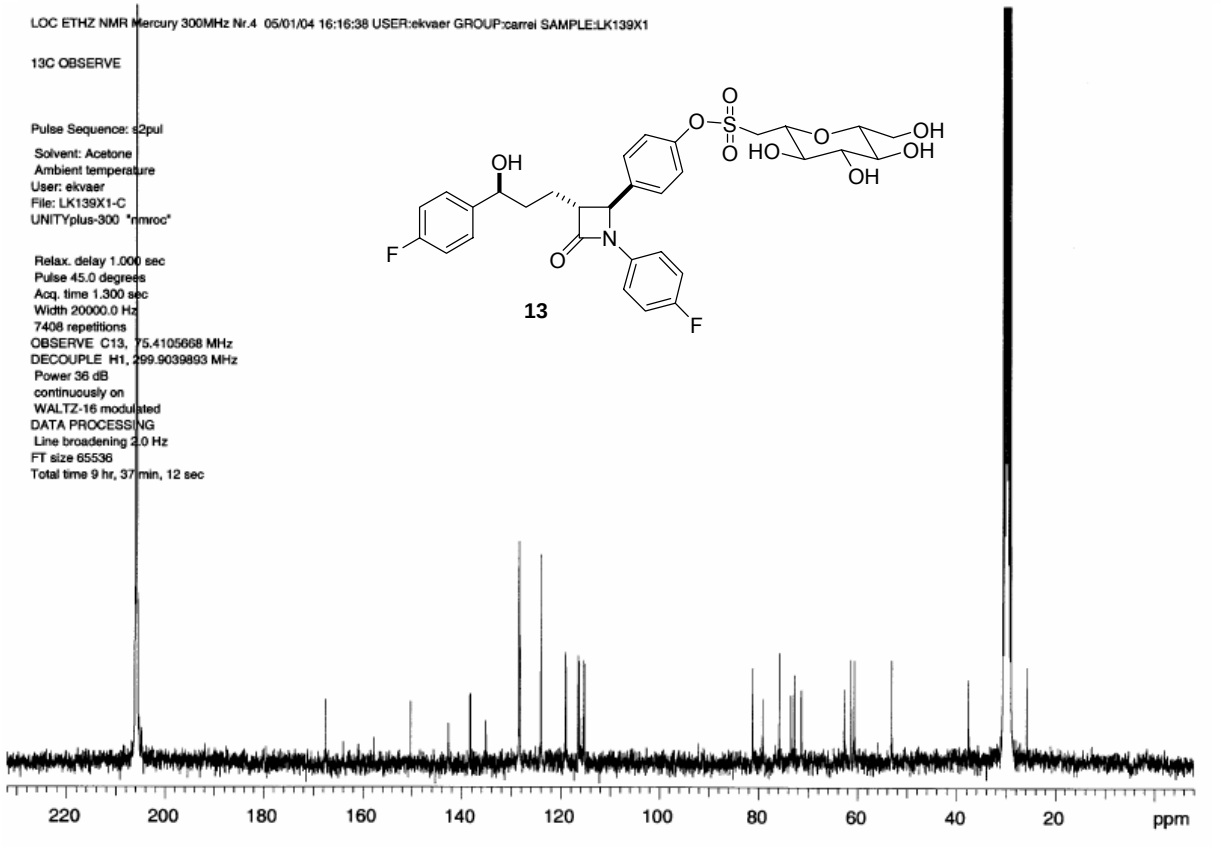

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:05:38 USER:ekvaer GROUP:carrei SAMPLE:LK135X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK135X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2246216 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
12
9 8 7 6 5 4 3 2 1 0 ppm
5.43 10.15 15.57
1.02
2.48 5.11 5.13 10.69 5.64 7.65 2.69 5.51 6.17
12.93
2.26 1.55

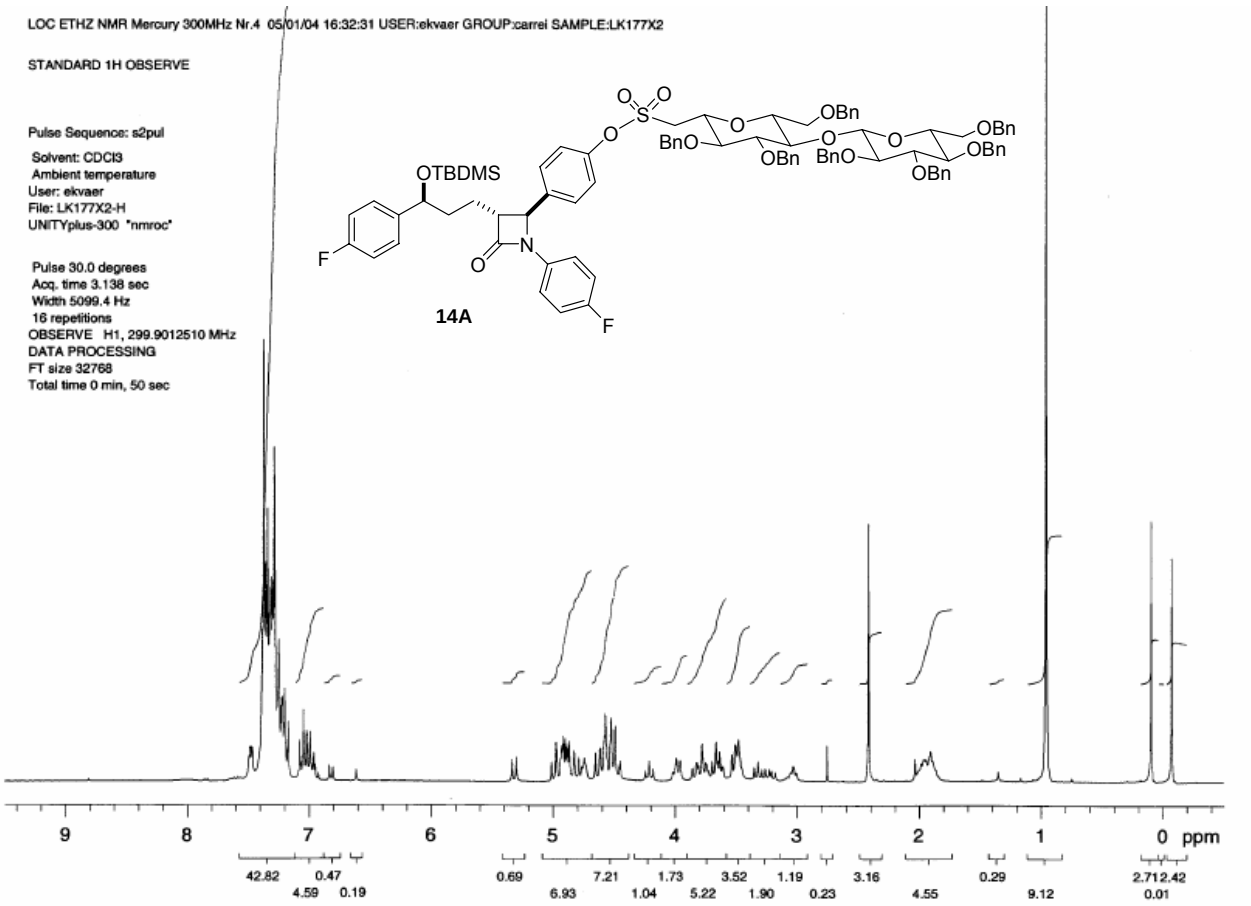

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:06:17 USER:ekvaer GROUP:carrei SAMPLE:LK135X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK135X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
500 repetitions
OBSERVE C13, 75.4914917 MHz
DECOUPLE H1, 300.2258037 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 19 min, 14 sec
12
220 200 180 160 140 120 100 80 60 40 20 ppm

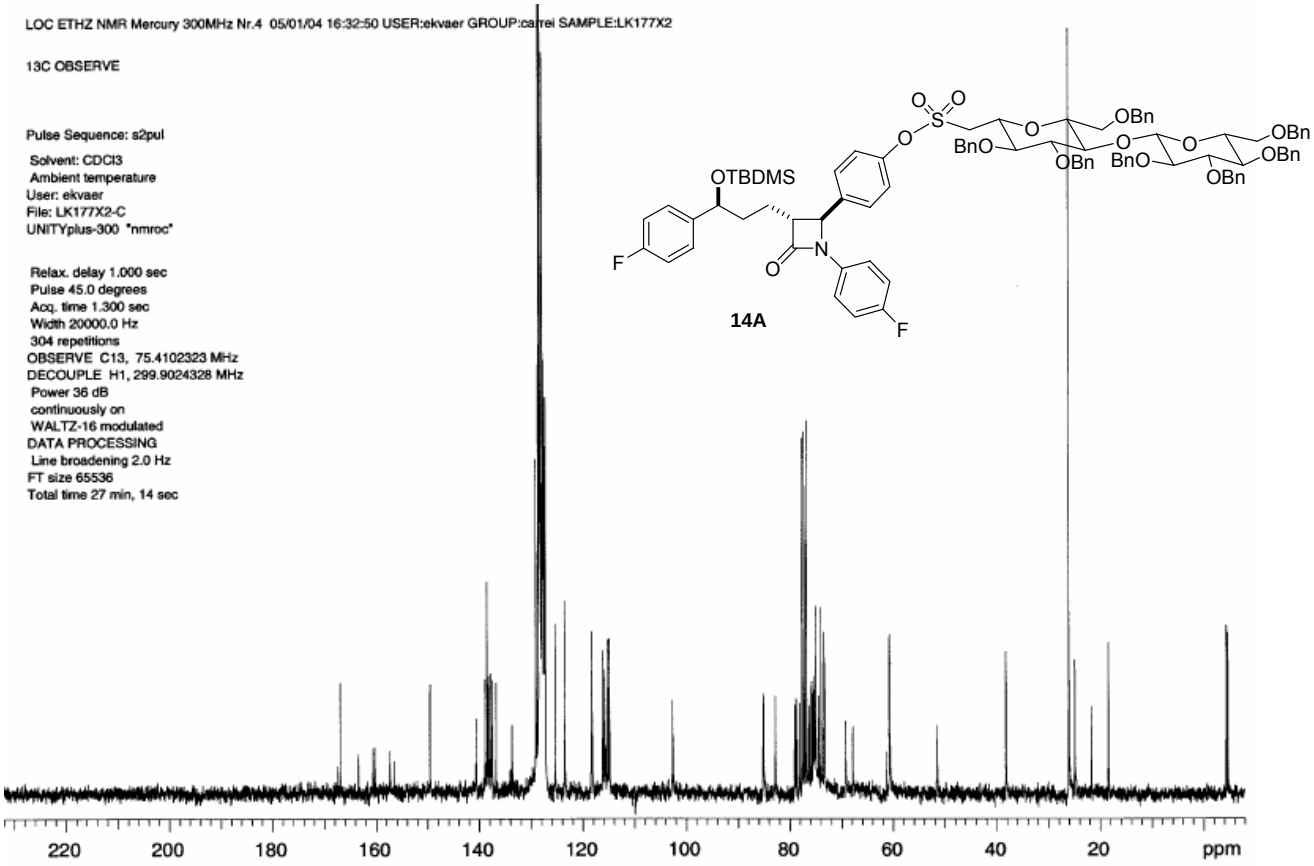

LOC ETHZ NMR Gemini 300 MHz Nr.3 05/01/04 16:14:43 USER:ekvaer GROUP:carrei SAMPLE:LK116X3
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK116X3-H
UNITYplus-300 "nmroc"
Pulse 29.5 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.0836333 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
F
O
N
F
13A
OBn
OBn
OBn
BnO
9
8
7
6
5
4
3
2
1
0 ppm
39.97
5.98
5.42
8.52
1.28
5.66
4.22
1.39
1.32
5.48
12.92
3.73
4.11

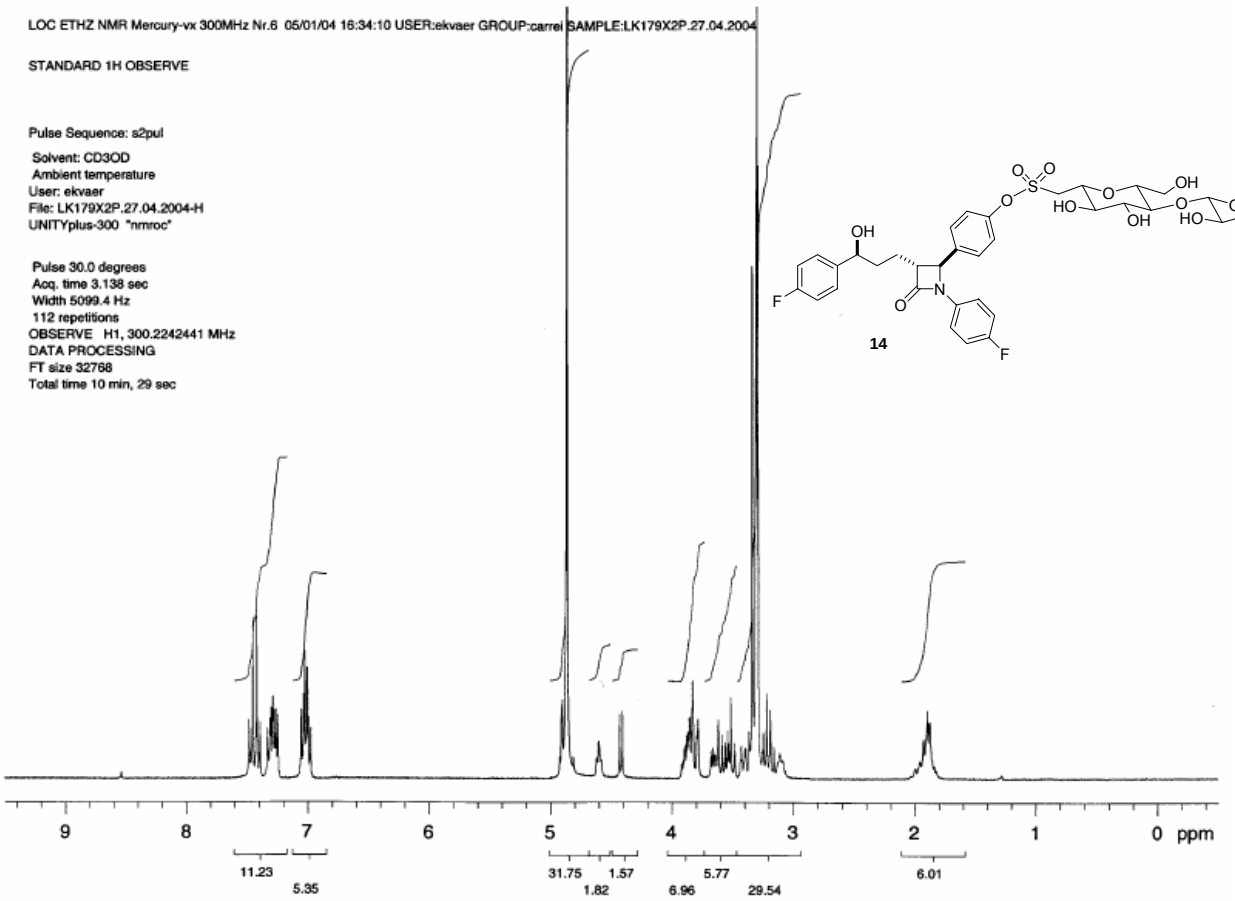

LOC ETHZ NMR Gemini 300 MHz Nr.3 05/01/04 16:15:05 USER:ekvaer GROUP:carrei SAMPLE:LK116X3
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK116X3-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
64 repetitions
OBSERVE C13, 75.4560752 MHz
DECOUPLE H1, 300.0848347 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 2 min, 27 sec
OTBDMS
F
O
N
F
13A
OBn
OBn
OBn
BnO
220
200
180
160
140
120
100
80
60
40
20
ppm

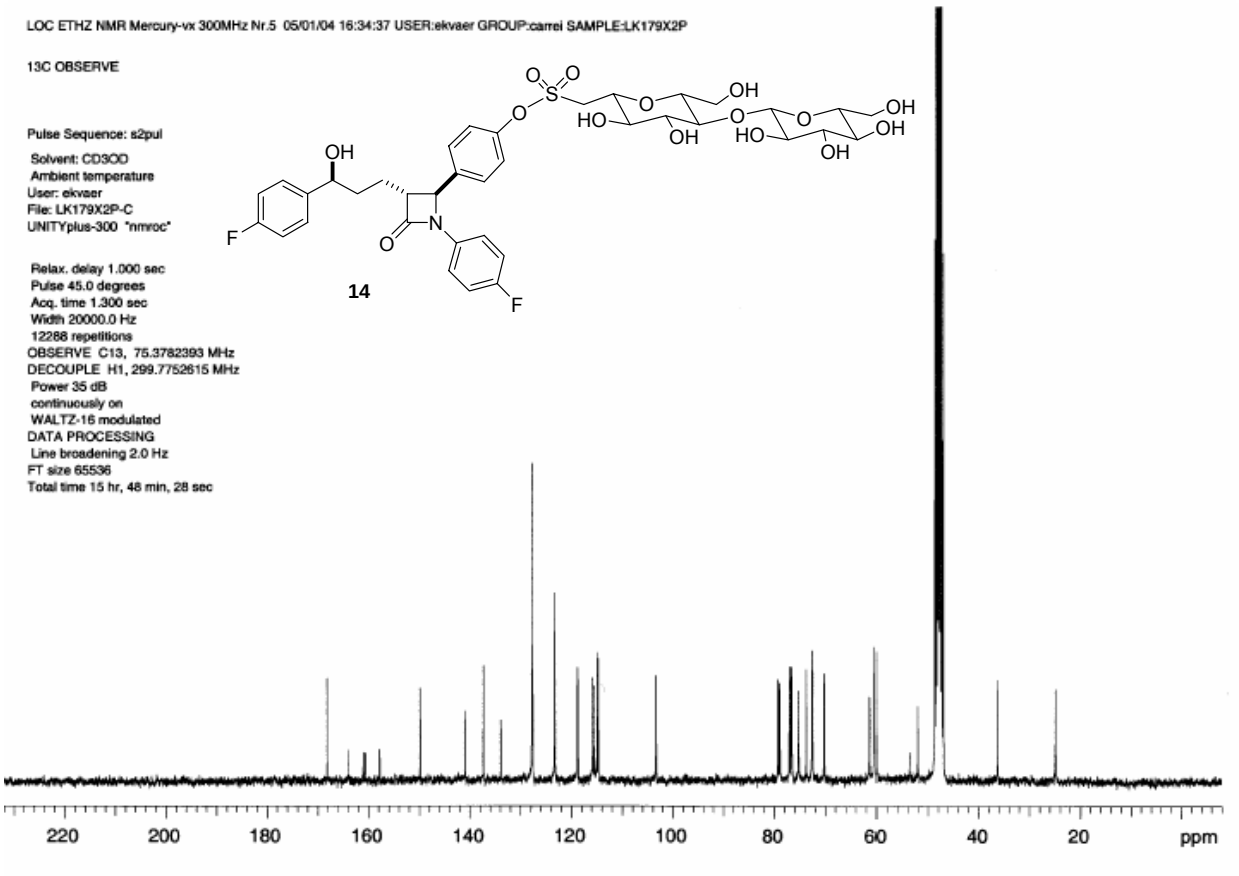

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:16:19 USER:ekvaer GROUP:carrei SAMPLE:LK139X2
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CD3OD
Ambient temperature
User: ekvaer
File: LK139X2P-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9024335 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
13
9 8 7 6 5 4 3 2 1 0 ppm
7.80 7.00 7.18 2.53 19.89 1.75 2.03 20.60 18.88 4.32 8.02

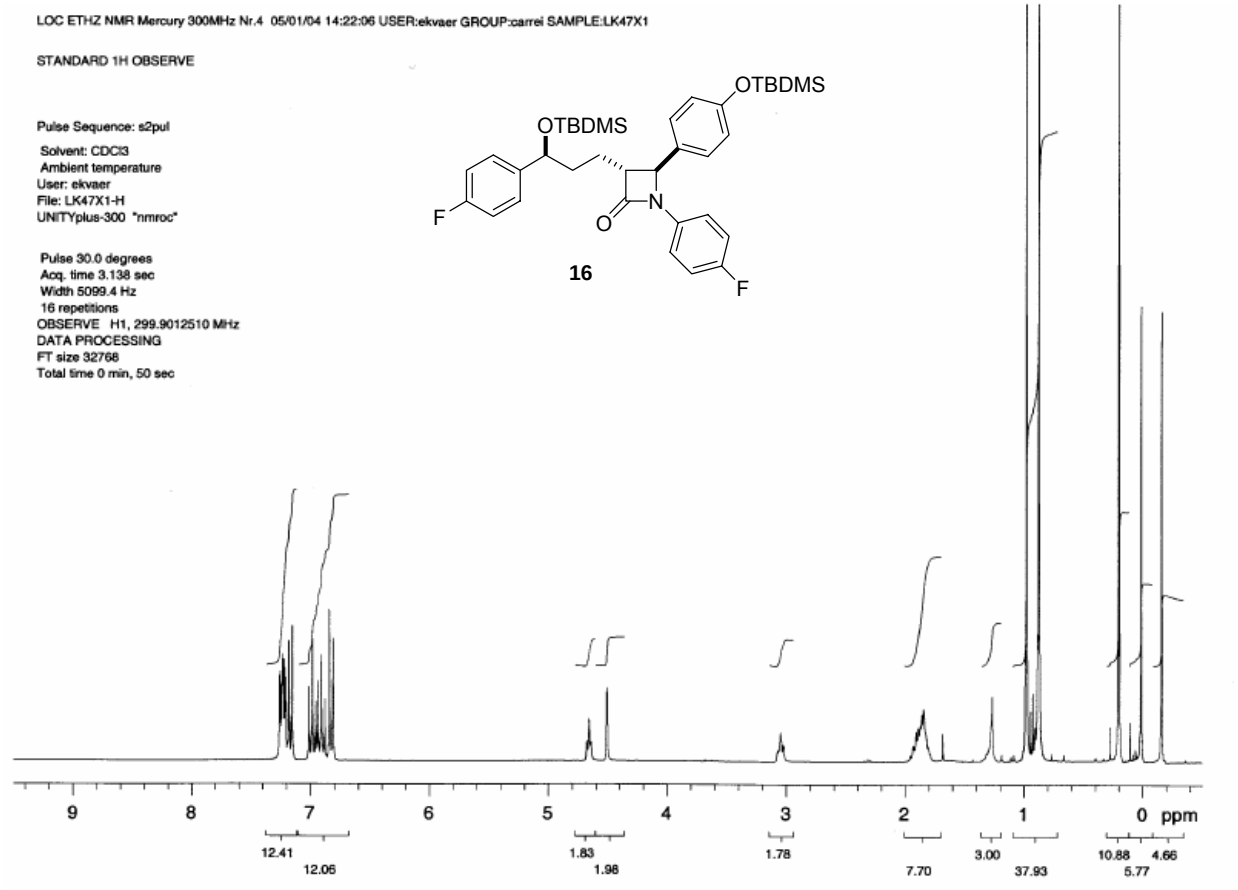

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:16:38 USER:ekvaer GROUP:carrei SAMPLE:LK139X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK139X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
7408 repetitions
OBSERVE C13, 75.4105668 MHz
DECOUPLE H1, 299.9039893 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 hr, 37 min, 12 sec
13
220 200 180 160 140 120 100 80 60 40 20 ppm

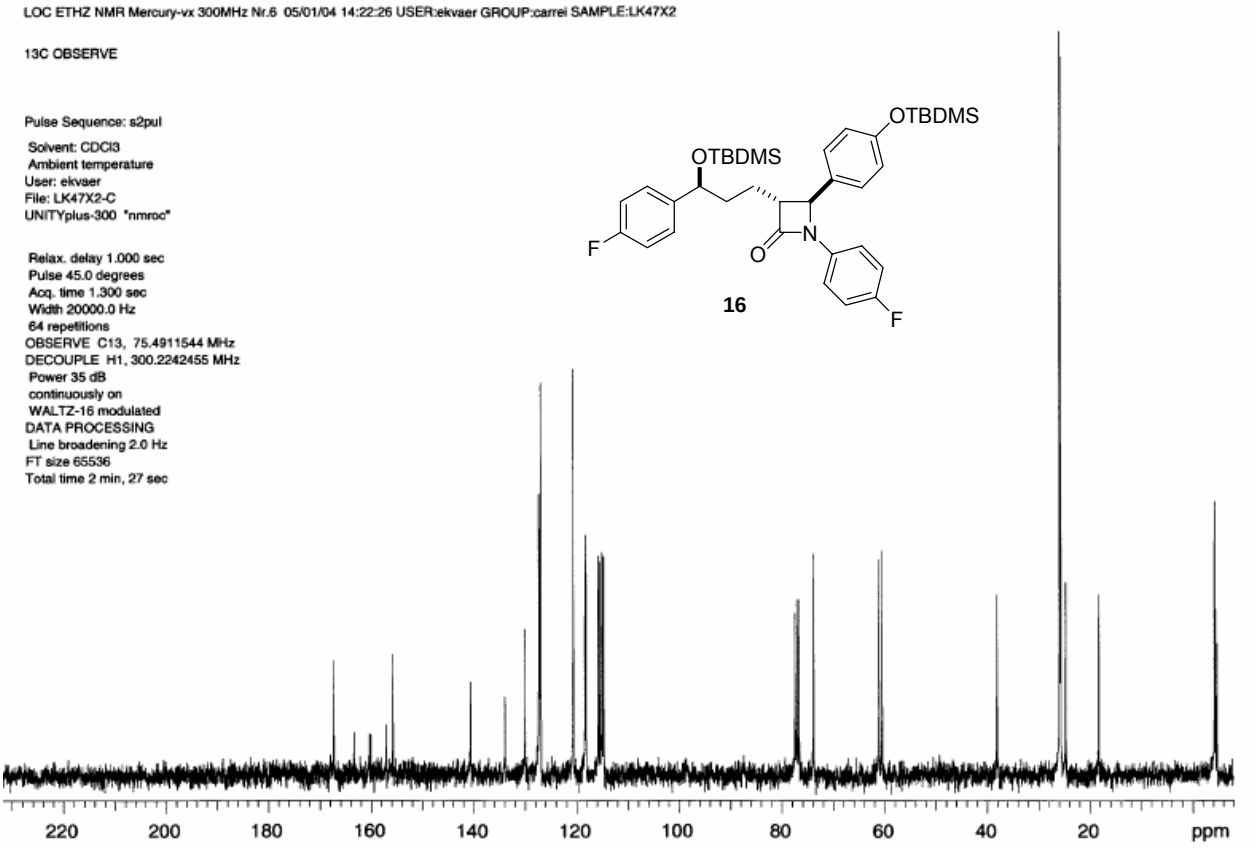

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:32:31 USER:ekvaer GROUP:carrei SAMPLE:LK177X2
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK177X2-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
F
O
N
O
F
14A
OBn
BnO
OBn
BnO
OBn
OBn
9
8
7
6
5
4
3
2
1
0 ppm
42.82
0.47
4.59
0.19
0.69
7.21
6.93
1.73
1.04
3.52
5.22
1.19
1.90
0.23
3.16
4.55
0.29
9.12
2.71
2.42
0.01

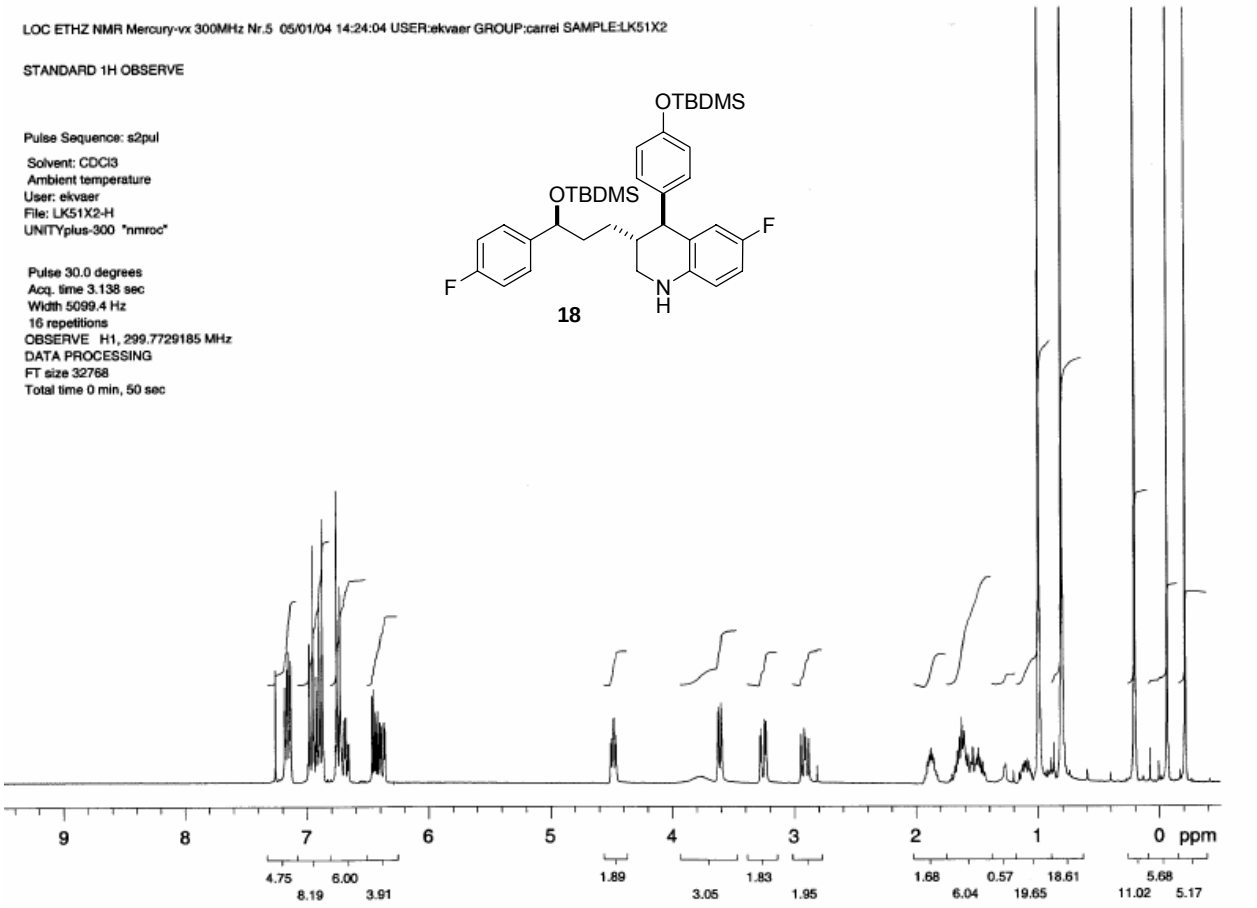

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 16:32:50 USER:ekvaer GROUP:carrei SAMPLE:LK177X2
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK177X2-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
304 repetitions
OBSERVE C13, 75.4102323 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 27 min, 14 sec
OTBDMS
F
O
N
O
F
14A
OBn
BnO
OBn
BnO
OBn
OBn
220
200
180
160
140
120
100
80
60
40
20
ppm

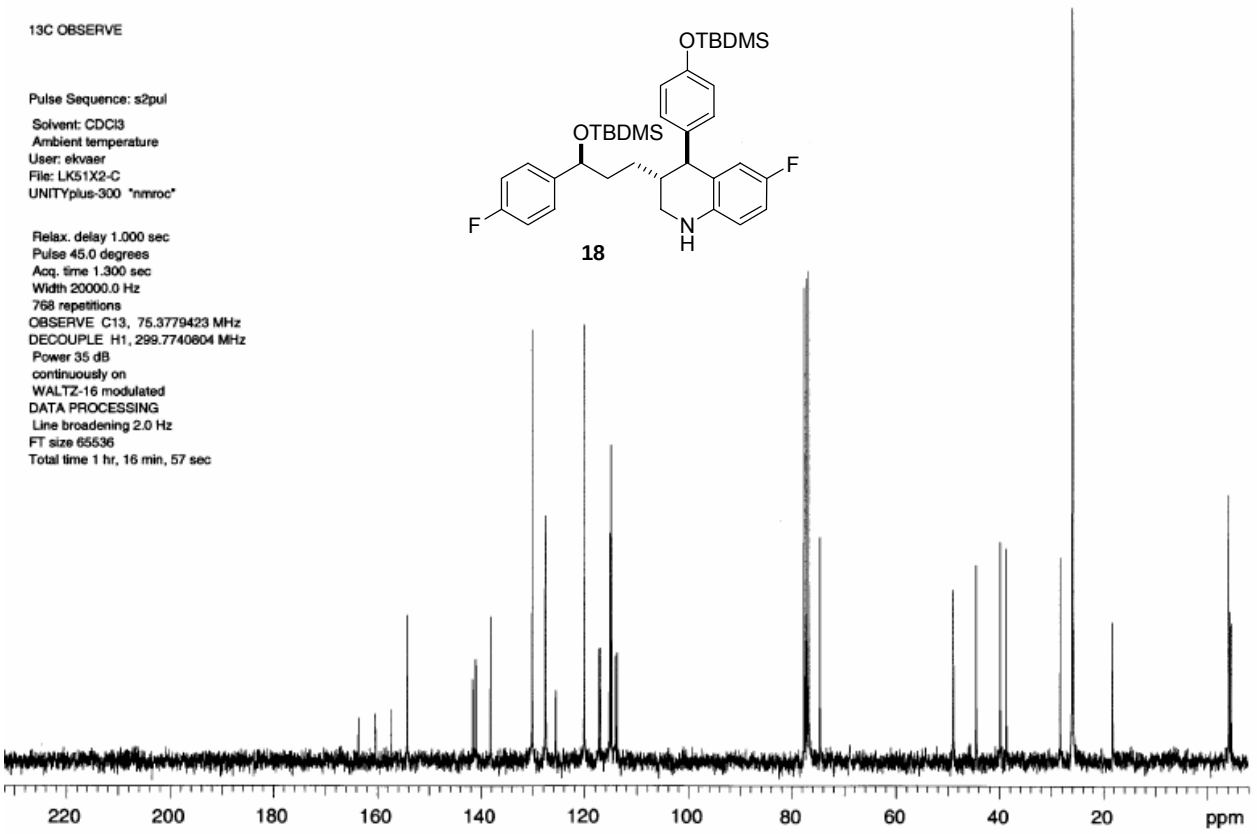

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:34:10 USER:ekvaer GROUP:carrei SAMPLE:LK179X2P.27.04.2004
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CD3OD
Ambient temperature
User: ekvaer
File: LK179X2P.27.04.2004-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
112 repetitions
OBSERVE H1, 300.2242441 MHz
DATA PROCESSING
FT size 32768
Total time 10 min, 29 sec
14
9
8
7
6
5
4
3
2
1
0 ppm
11.23
5.35
31.75
1.57
1.82
5.77
6.96
29.54
6.01

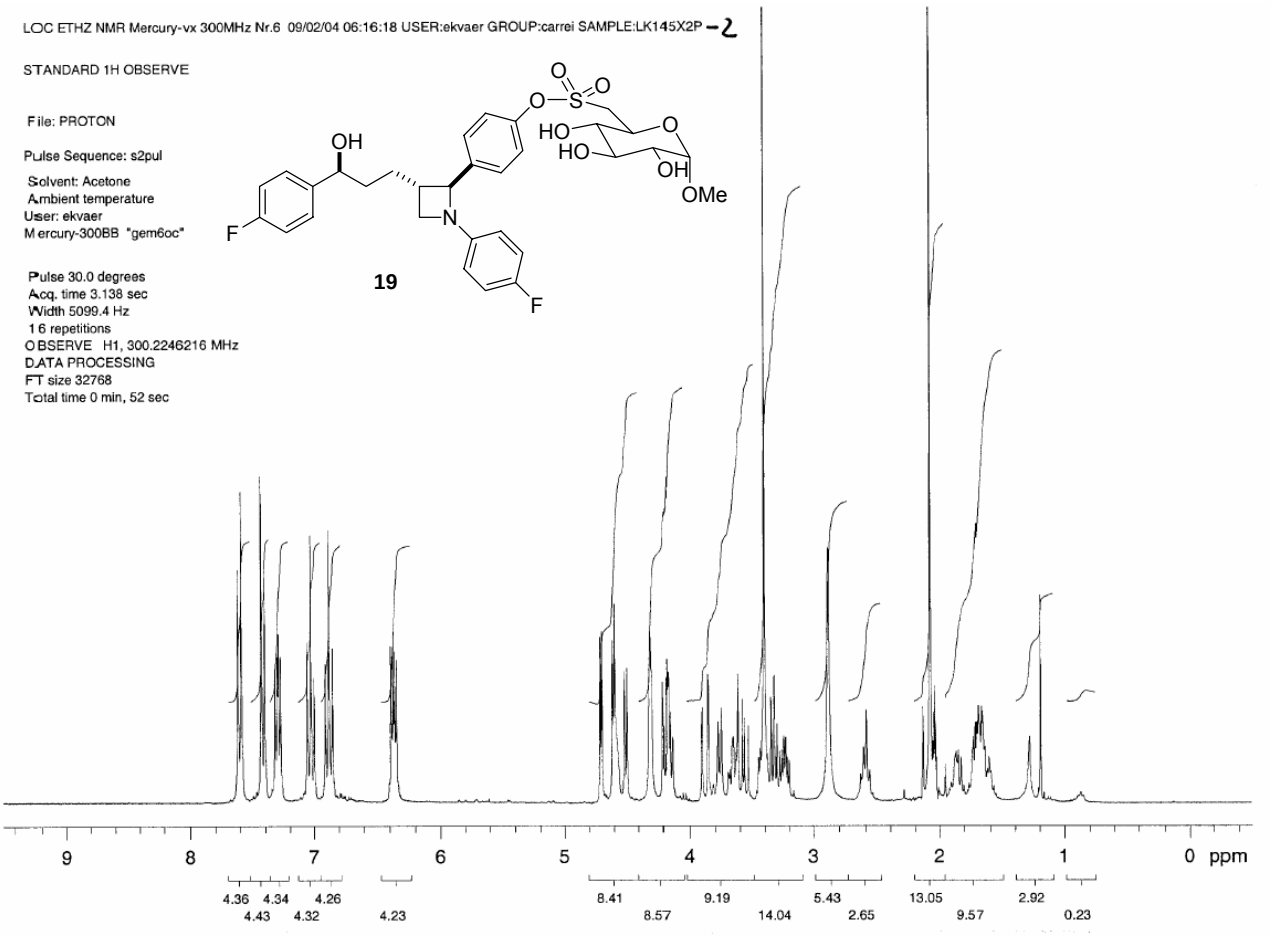

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 16:34:37 USER:ekvaer GROUP:carrei SAMPLE:LK179X2P
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CD3OD
Ambient temperature
User: ekvaer
File: LK179X2P-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
12288 repetitions
OBSERVE C13, 75.3782393 MHz
DECOUPLE H1, 299.7752615 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 15 hr, 48 min, 28 sec
14
220
200
180
160
140
120
100
80
60
40
20
ppm

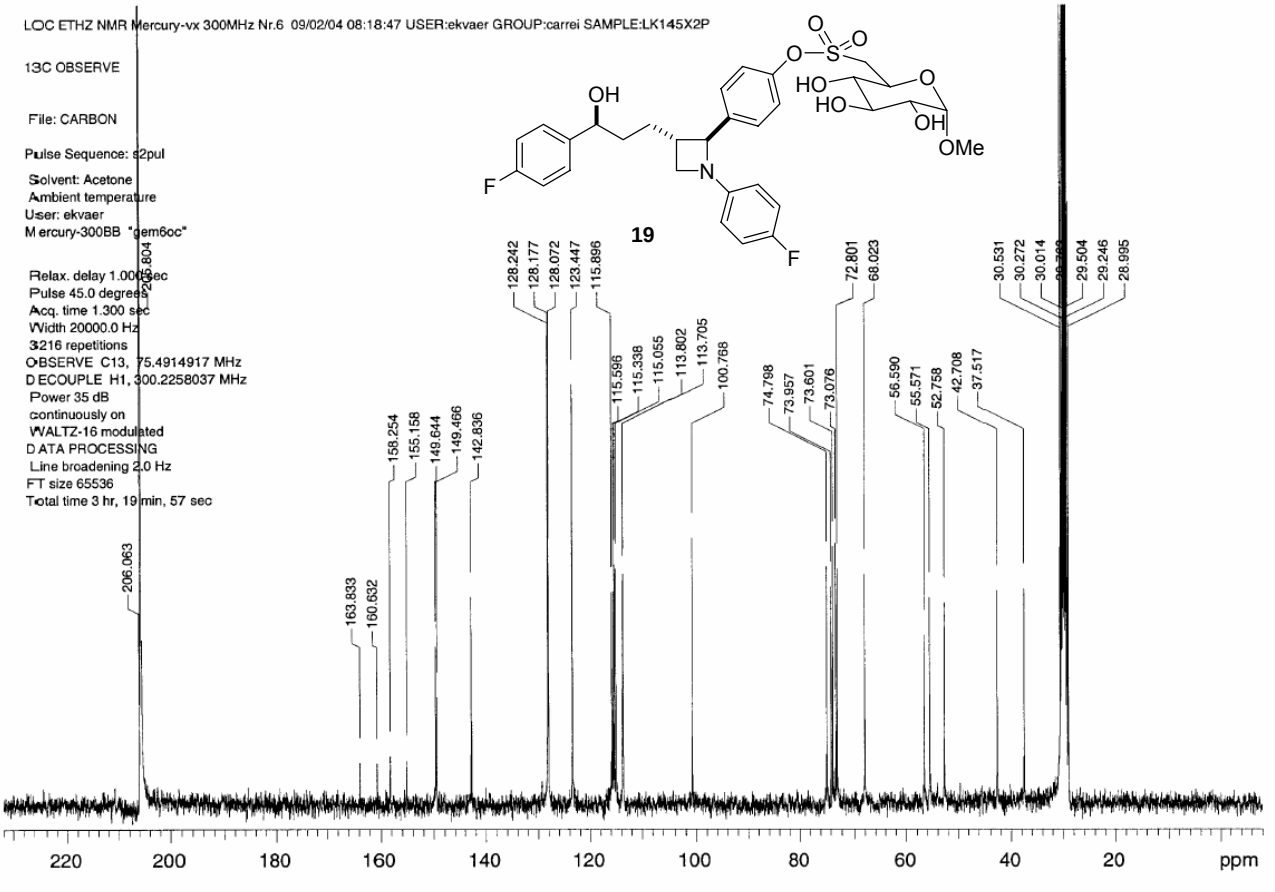

LOC ETHZ NMR Mercury 300MHz Nr.4 05/01/04 14:22:06 USER:ekvaer GROUP:carrei SAMPLE:LK47X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK47X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
OTBDMS
F
O
N
F
16
9
8
7
6
5
4
3
2
1
0 ppm
12.41
12.06
1.83
1.98
1.78
7.70
3.00
37.93
10.88
4.66
5.77

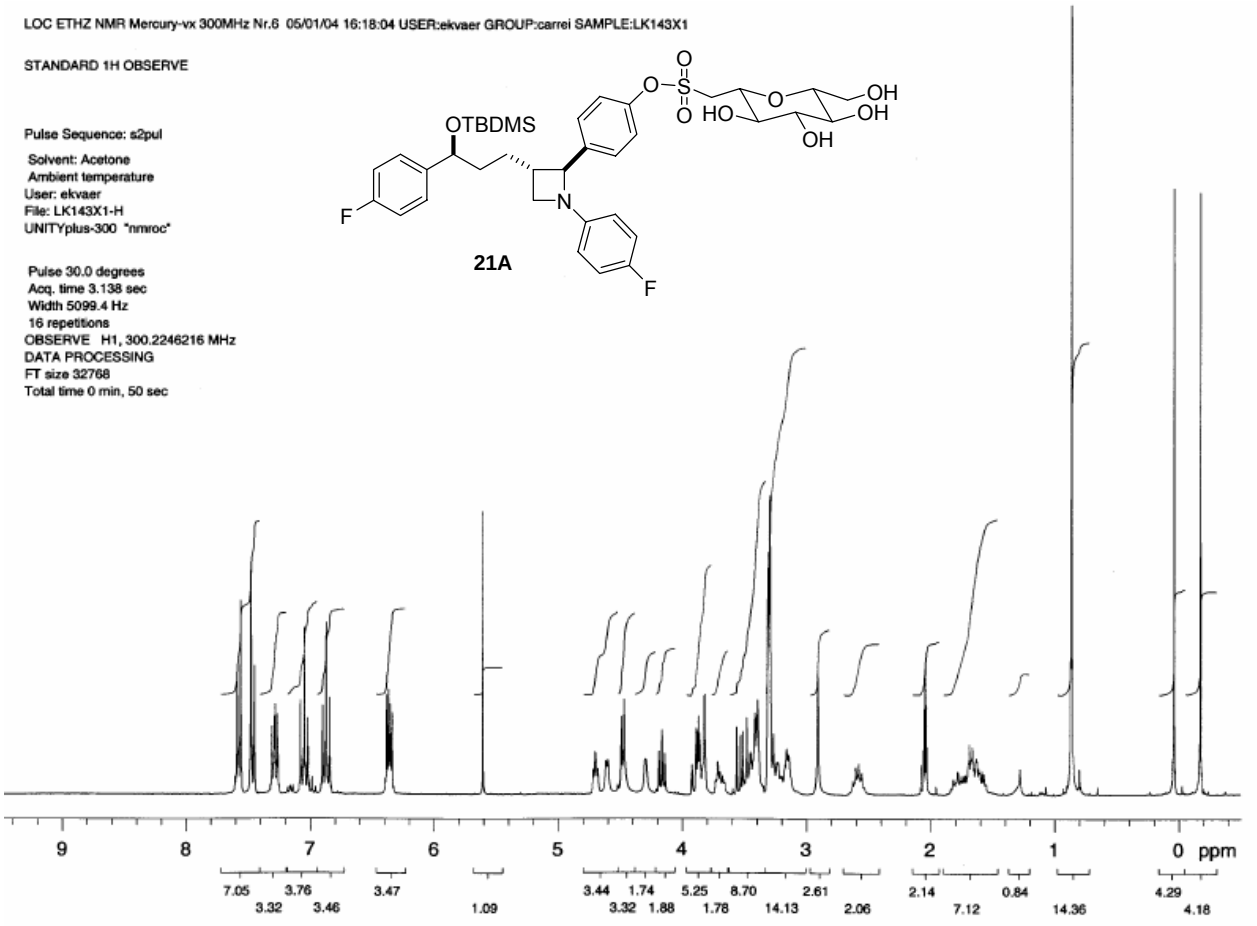

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 14:22:26 USER:ekvaer GROUP:carrei SAMPLE:LK47X2
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK47X2-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
64 repetitions
OBSERVE C13, 75.4911544 MHz
DECOUPLE H1, 300.2242455 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 2 min, 27 sec
OTBDMS
OTBDMS
F
O
N
F
16
220
200
180
160
140
120
100
80
60
40
20
ppm

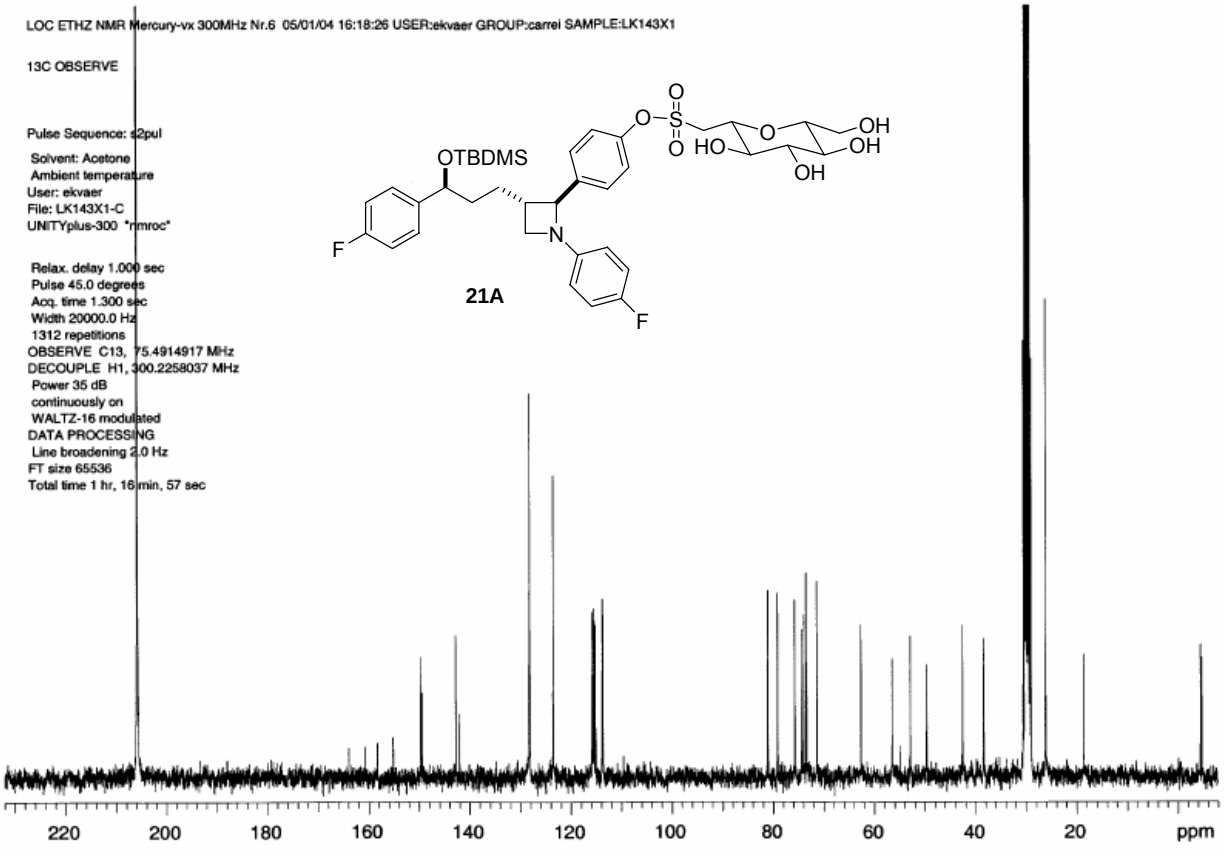

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 14:24:04 USER:ekvaer GROUP:carrei SAMPLE:LK51X2
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK51X2-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.7729185 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
OTBDMS
F
F
N
H
18
9
8
7
6
5
4
3
2
1
0 ppm
4.75
6.00
8.19
3.91
1.89
1.83
3.05
1.95
1.68
0.57
18.61
6.04
19.65
5.68
11.02
5.17

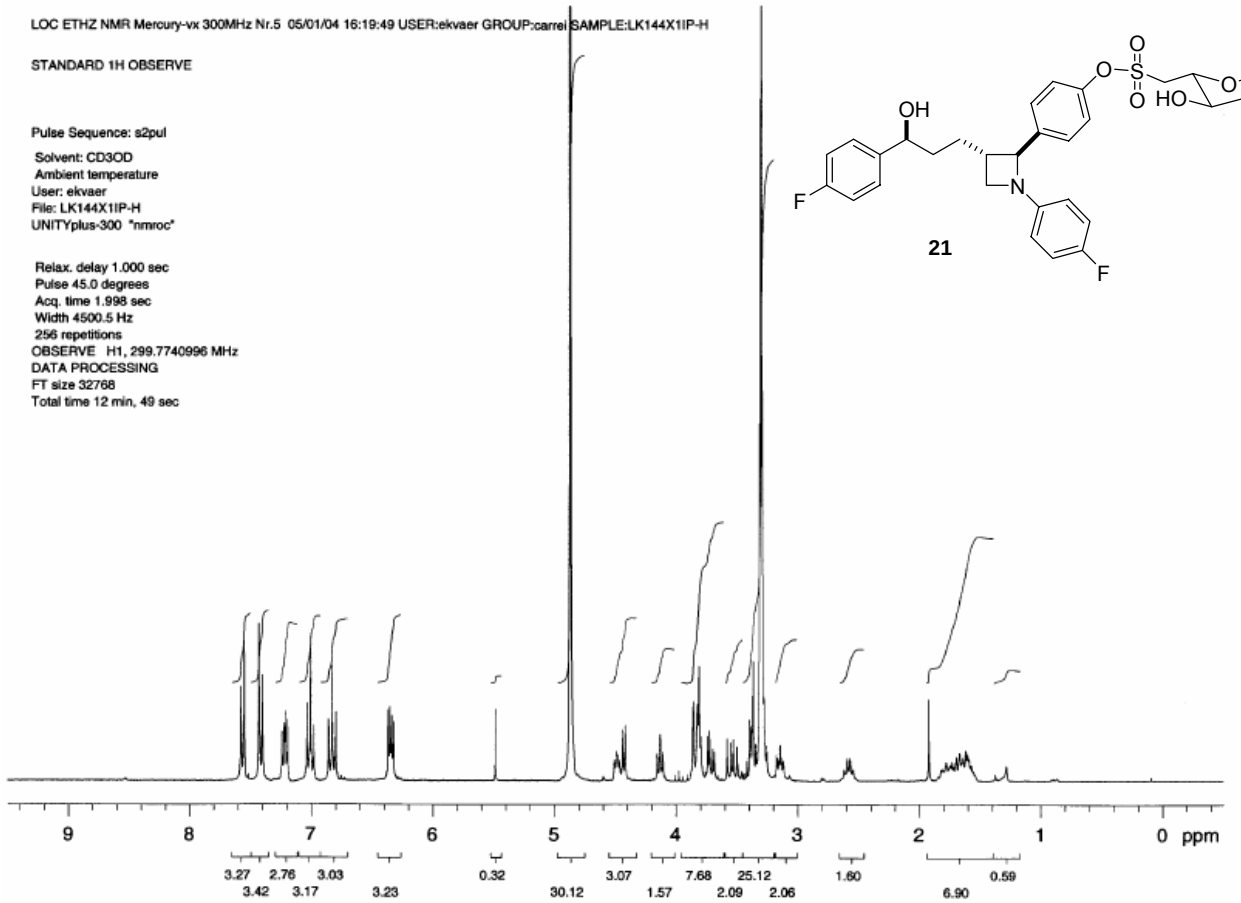

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 14:24:23 USER:ekvaer GROUP:carrei SAMPLE:LK51X2
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: ekvaer
File: LK51X2-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
768 repetitions
OBSERVE C13, 75.3779423 MHz
DECOUPLE H1, 299.7740804 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 16 min, 57 sec
OTBDMS
OTBDMS
F
F
N
H
18
220
200
180
160
140
120
100
80
60
40
20
ppm

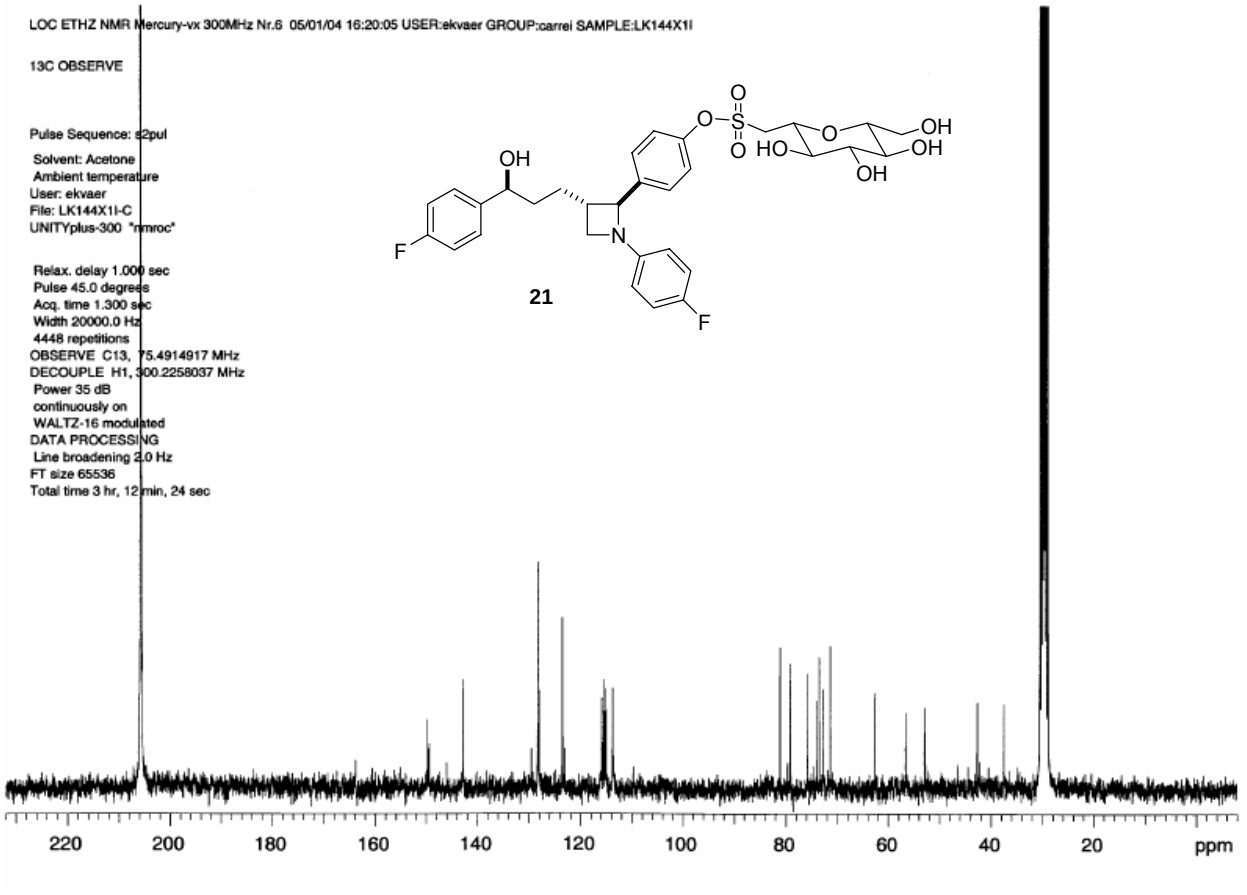

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 09/02/04 06:16:18 USER:ekvaer GROUP:carrei SAMPLE:LK145X2P
STANDARD 1H OBSERVE
File: PROTON
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
Mercury-300BB "gem6oc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2246216 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 52 sec
19
9 8 7 6 5 4 3 2 1 0 ppm
4.36 4.34 4.26
4.43 4.32 4.23
8.41 9.19 5.43 13.05 2.92
8.57 14.04 2.65 9.57 0.23


LOC ETHZ NMR Mercury-vx 300MHz Nr.6 09/02/04 08:18:47 USER:ekvaer GROUP:carrei SAMPLE:LK145X2P
13C OBSERVE
File: CARBON
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
Mercury-300BB "gem6oc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
3216 repetitions
OBSERVE C13, 75.4914917 MHz
DECOUPLE H1, 300.2258037 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 3 hr, 19 min, 57 sec
19
206.804
206.063
163.833
160.632
158.254
155.158
149.644
149.466
142.836
128.242
128.177
128.072
123.447
115.896
115.596
115.338
115.055
113.802
113.705
100.768
74.798
73.957
73.601
73.076
72.801
68.023
56.590
55.571
52.758
42.708
37.517
30.531
30.272
30.014
29.504
29.246
28.995
220 200 180 160 140 120 100 80 60 40 20 ppm


LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:18:04 USER:ekvaer GROUP:carrei SAMPLE:LK143X1
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK143X1-H
UNITYplus-300 "nmroc"
Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2246216 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
OTBDMS
F
N
F
O
S
O
O
HO
O
OH
OH
OH
21A
9
8
7
6
5
4
3
2
1
0 ppm
7.05
3.76
3.32
3.46
3.47
1.09
3.44
1.74
3.32
1.88
5.25
8.70
1.78
14.13
2.61
2.06
2.14
7.12
0.84
14.36
4.29
4.18


LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:18:26 USER:ekvaer GROUP:carrei SAMPLE:LK143X1
13C OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK143X1-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
1312 repetitions
OBSERVE C13, 75.4914917 MHz
DECOUPLE H1, 300.2258037 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 16 min, 57 sec
OTBDMS
F
N
F
O
S
O
O
HO
O
OH
OH
OH
21A
220
200
180
160
140
120
100
80
60
40
20
ppm


LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/01/04 16:19:49 USER:ekvaer GROUP:carrei SAMPLE:LK144X1IP-H
STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CD3OD
Ambient temperature
User: ekvaer
File: LK144X1IP-H
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
256 repetitions
OBSERVE H1, 299.7740996 MHz
DATA PROCESSING
FT size 32768
Total time 12 min, 49 sec
21
9 8 7 6 5 4 3 2 1 0 ppm
3.27 2.76 3.03 0.32 3.07 7.68 25.12 1.60 0.59
3.42 3.17 3.23 30.12 1.57 2.09 2.06 6.90


LOC ETHZ NMR Mercury-vx 300MHz Nr.6 05/01/04 16:20:05 USER:ekvaer GROUP:carrei SAMPLE:LK144X1I
13C OBSERVE
Pulse Sequence: s2pul
Solvent: Acetone
Ambient temperature
User: ekvaer
File: LK144X1I-C
UNITYplus-300 "nmroc"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
4448 repetitions
OBSERVE C13, 75.4914917 MHz
DECOUPLE H1, 300.2258037 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 3 hr, 12 min, 24 sec
21
220 200 180 160 140 120 100 80 60 40 20 ppm